Chemistry and Physics of Surfaces and Interfaces
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Lecture - 26
Imaging Molecules and Atom Manipulation on Surfaces

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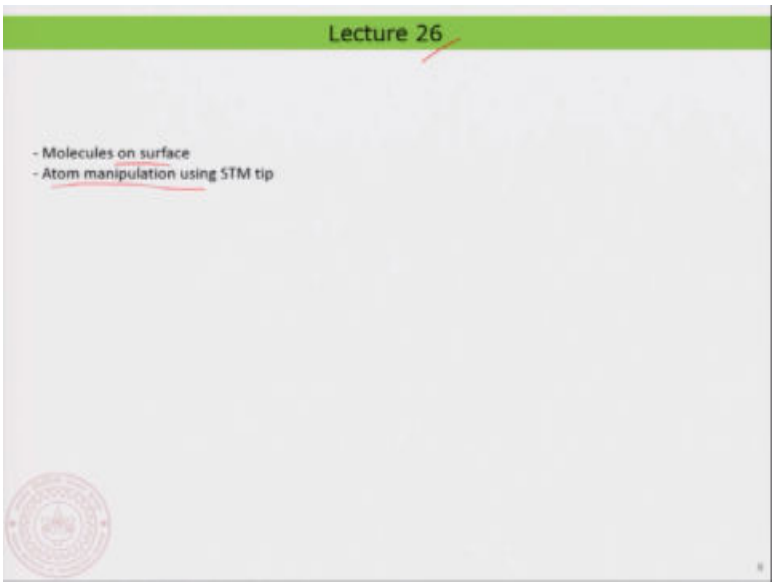

Hello, everyone, welcome back. So, in this lecture 26, we will continue LL with more on this molecule on surface, we have already seen a couple of example, but I will show you a few more examples and also look at what happens really at the interface and also when you grow thicker layers. And then we will actually get into something like a new prospect or of surface science. And also one of the most important aspect about scanning tunneling microscopy, which is actually known as atom manipulation. So, this is very interesting topic. We will also cover within this lecture, good.

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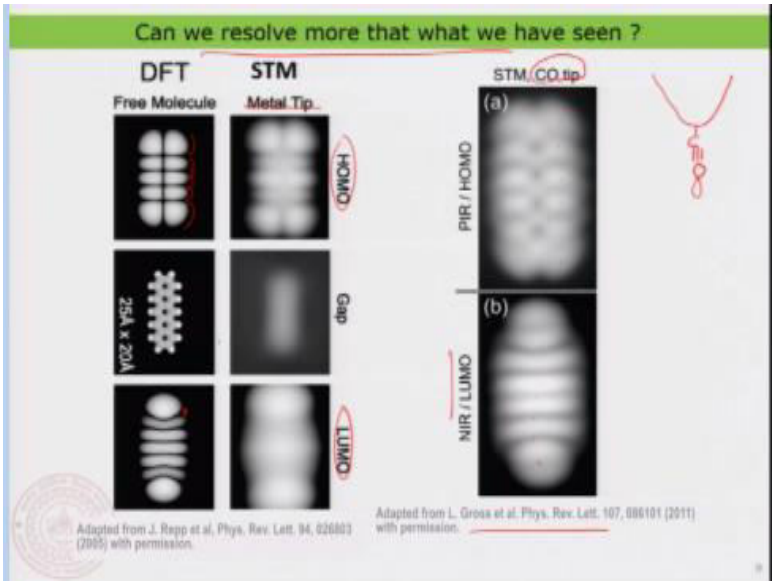

So, what we have seen was basically that we can resolve the molecular orbitals depending on the bias that you apply, you are actually imaging the homo or lumo of the molecule. So, this was nice. Now the question is can we resolve a bit more than this? Yeah, we are always ambitious; So, that is very clear. So, that is the reason why we are actually just studying something of this interesting that ambition actually make us or put us in a question, can we resolve something more than that? Or can we really resolve the molecular orbital as we theoretically predict? Well, you see that when I do that with a metal tip, well, I can kind of reproduce the homo, but the lumo is not that clearly reproduced so that means the tip that I am using, the metallic tip that I am using is probably not able to really get into these tiny space here. Because you know that the molecule itself is about one nanometer, it is not more than that. So that means if I want to resolve these kind of tiny features that are within the molecular orbital, my sharpness or the sharpness of the tip should also be in that order. So, probably, although we talk about a sharp metallic tip, it is not necessary that you are always looking, you are always having an idealized, one atom tip. So that is the interesting aspect. But well, it also has a few additional aspect that metallic tip also known to have kind of a broad density of state. Therefore, they are not electronically sharp. So that is also the interesting point So, therefore, people thought, well, we can actually just use some kind of a molecule to scan an image to a next resolution. So, what they have done is in this paper, you can see that they have actually used a carbon monoxide tip. So, what do you have is you have a tip like this. And a carbon monoxide is basically sitting like this. Now, you see that you have a sharp atom that is sitting next to it. And it also has some kind of a strong p kind of state, which is also protruding along the axis of the molecule. So that actually makes something about the carbon monoxide itself. And therefore, you could expect that the carbon

monoxide tip could resolve something more. Well, that is exactly what you are seeing here. Now, you can see that I have 1, 2, 3, 4, 5, 6. And that is exactly what you are seeing here, you can basically just almost count the same number of density of state, same density as you would see here in the theory. So, you can almost reproduce and also more striking is actually the lumo of the molecule. So, you can see now. I can see exactly the same type of contrast. And here I have basically 1, 2, 3, 4, 5, nodes. And that is exactly what I also see here 1, 2, 3, 4, 5, 6. Well that means one more here. So that is the interesting aspect about it. So, you can basically almost get the copy of the molecular orbital using a carbon monoxide tip. So that is very, very interesting. So that means we can really resolve down to the electronic structure at its highest resolution possible.

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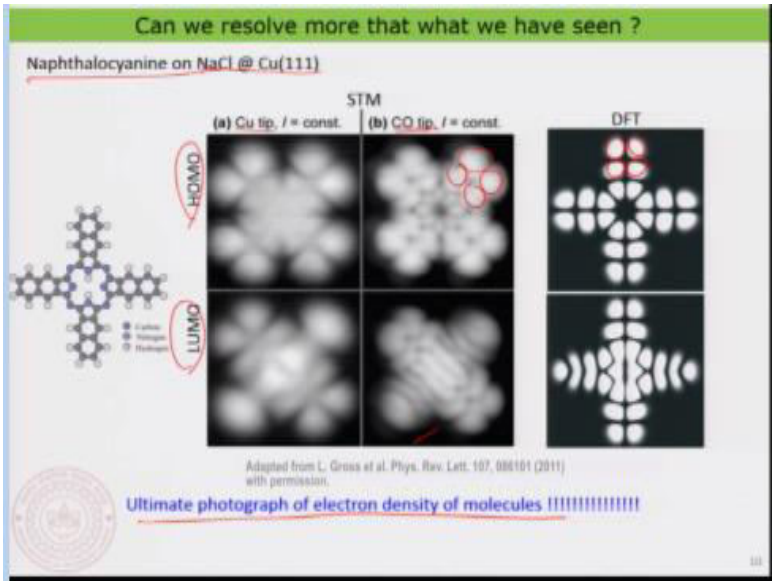

Well, I have one more example here. This is again that naphthalocyanine in molecule. Here again, the interesting thing you would always notice that this is sitting on a layer of sodium chloride on the metal surface. And you can also see that depending on the bias voltage, you can image the homo or the lumo. And here, they have actually compared the copper tip and the CO tip. So, with the copper tip, you see like you can resolve to a good extent, but not as you would expect in the density functional theory or in the theoretical calculation. So, you can however, when you use a carbon monoxide tip that means a sharpest tip that you can think of, you can clearly reproduce these lobe as you see in the theoretical calculations. So, this is quite spectacular also the same with the unfilled orbital, you can also clearly reproduce the contrast as you would expect from a theoretical calculation. So, this is really, really amazing. So, what you are seeing ideally is the ultimate photograph of the electron density of a molecule at different energies. Now, that is also the interesting thing. The electron density

is also changing depending on which molecular orbital you are looking at; So the electron density is clearly different So that is something that you are basically meshing. So you have basically the STM, therefore has the capability to go down with the resolution down to this level. So that is the power of the technique and always we are doing at a single molecule level.

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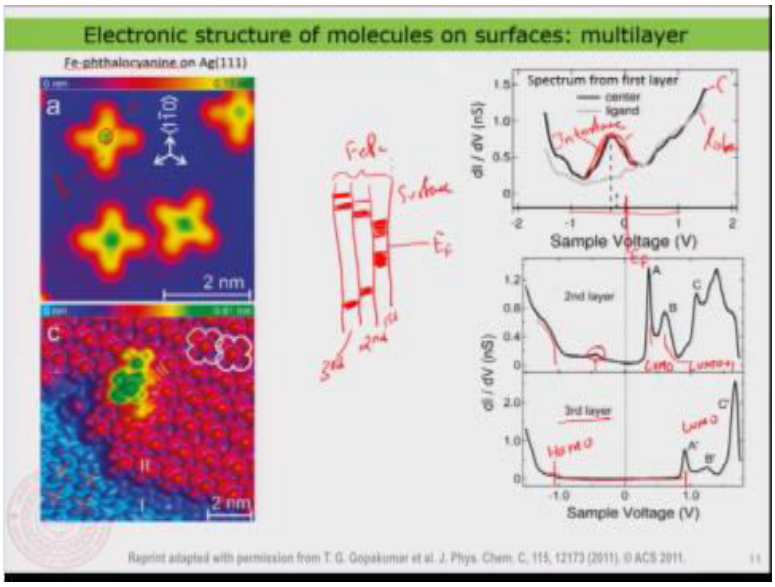

But now what we want to do is also we want to understand the electronic structure as a function of the layer thickness. So, so far, what I have shown you is the electronic structure of the molecule which is taking on the first layer. So that is the thing that we have so far looked, but now, I want to take you to another perspective. Now, this molecule we have already discussed. So; this is the iron phthalocyanine. So, this is taking on silver 111 surface.

Now, you see, in this particular example, I do not have that sodium chloride in between. So that is also something I have already told you to just keep it in mind. So, I do not have that sodium chloride. So, this molecule is directly sitting on a silver surface. Now, if you look at the spectrum, the spectrum of course, taken at the center of the molecule and also at the lobe of the molecule, so this is taken at the center. And this is actually taken at the lobe that means one spectrum is recorded here. This is actually the center and this is basically the lobe of the molecule. So that is the point. So, it is a tunneling spectroscopy. So, you can basically just place your tip in the center of the molecule and record the spectrum or you can basically record it at the arm of the molecule or the lobe of the molecule.

But now, when you look at the spectrum, it is not looking same as what we have seen in the previous cases. It is looking quite different. And it actually has quite some density even in this region around the Fermi level. And also it has a very, very strong state, as you see here, near the Fermi level. So, this is basically the Fermi level and it has a very strong state even near the Fermi level. So, now well, what is actually happening? So, this is quite interesting. So, what is so different for this molecule compared to the molecule that you have actually just seen in the previous lecture. So, now that is where the sodium chloride plays the role. Now, the point is, when a molecule just goes on to the surface, it is not necessary that the molecule is just taking on the surface. It is actually that the molecules do kind of chemical interaction between the surface particularly when you have metallic centers that metal would actually interact with the surface metal and then they would actually just make a new bonding between the molecule and the surface. So that means the molecule is not really chemisorbed as in the case of a carbon monoxide serving on the surface. But the iron is actually interacting with the gold and they are actually just making some kind of a chemical interaction. So that chemical interaction means there is a charge transfer between the molecule and the surface or from the surface to the molecule depending on the interaction. And because of this kind of interaction, you will basically get these kind of stayed close to the Fermi energy, which is actually some kind of an interfacial state. So, this is basically a state that you would only find at the interface.

Now, you would ask, why did not I see that in the case of the phthalocyanine, in that we have looked at? That actually, because you have sodium chloride layer in between the molecule and the surface. And the sodium chloride actually act as an insulator, which would basically limit the interaction of the molecule with the surface. So, there, it was a purpose, because you wanted to clearly measure the electronic states of the molecule. So, if the molecule interacts with the surface, you cannot do that. And that is the reason why in those particular example, people did put an insulating layer in between the molecule and the surface and therefore, the electronic coupling between the molecule and the surface reduces or the chemical interaction between the molecule and the metal decreases. And therefore, you could basically see a nice gap between the homo and lumo. And you could see nice peaks that are corresponding to the homo and lumo and also the lumo + 1 and homo – 1 and so on that is Interesting thing. So, but here as soon as you put the molecule on a pure metallic surface, there are strong chemical interaction and these are actually the effect of the interface. So, this is also indicating that

there is a true chemical interaction going on and this kind of state would emerge when the molecule is really interacting with the surface.

But, you also might have noticed that in the case of molecule on graphite, you could also nicely see a region without any density of state that actually indicate that graphite is kind of a neutral surface. This is also very well known; because of the type of electronic structure, graphite is known to be kind of a neutral surface and when you put molecules on graphite, there is no true electronic interaction or there is no true chemical interaction between the molecule and the surface. And therefore, the molecule remains like in its normal state. That is the reason why you could basically see that the nice electronic gap between the homo and lumo of the molecule that you have deposited on the graphite surface. But now; let me just show you something interesting. Now, I have deposited this molecule on the metallic surface directly and you see the interface state which is actually the product of the interaction between the molecule and the surface.

Now, let me show you something interesting, because you recollect that we had also just deposited multi-layer of this molecule on the same. So, where I have the first layer, so, you recollect this I suppose and then I have actually the first layer and then I deposited the second layer and I even have a molecule here in the third layer. So, this would be the third layer so, the third layer of the molecule. And now, we can do is we can do basically measure the spectrum at the center of the molecule. And we can basically see what happens. So, now, something spectacular happens. You clearly see that there are peak like structures, like you have seen in the previous spectrum, in the case of the phthalocyanine, for example or the naphthalocyanine that we have looked at. Why is that? So that means the first layer, which is actually kind of an interfacial layer, which strongly interact with the surface is actually acting as some kind of a layer which decouples the second layer of the molecule from the metallic surface, because the molecule-molecule interaction is not as strong as the molecule metal interaction. So, therefore, the first layer of the molecule kind of act as a buffer layer, we call it or kind of a layer, which decouples the second layer from the metallic surface.

And therefore, you can clearly see that you have here the lumo and you have here, the lumo + 1 and so on. But now on the negative side that means the field orbital, you clearly see that it looking like more or less at a shoulder, is not as shoulder as on the unfilled states. But you also see that this state is still present that is actually the interfacial state, which is still not

vanished completely, because the molecule still has some kind of an influence with the surface. But as soon as you make the third layer that means this particular isolated molecule, here are a few molecule, then you clearly see that there is no interfacial or interface state, it is completely flat in this region. And then this is again, the lumo of the molecule. And here has some way, you can see the homo of the molecule. Now, you can see that the band gap or the homo-lumo gap that you are basically just seeing is kind of matching also with the expectation value of the electronic band gap of this kind of a molecule. I mean, this is iron phthalocyanine molecule. So that is nice. That basically means that the first layer is acting as some kind of a buffer layer. And the second layer is almost like the neutral molecule or the normal molecule like you would expect in the gas phase. And then the third layer is really like an isolated molecule. So that is something quite important because here also, you can see how the interfacial electronic structure works. So, if I would just put this is basically by metal. This is where the Fermi level of the metal. And you know, the first electronic state of the molecule is somewhat very broad. So, you can actually just mark it like a broad state here.

And then this is actually the first layer, first layer of the molecule and the second layer of the molecule, the third layer of the molecule and the first layer, you see that everything changes, it actually goes like that. And then the third layer, things are more or less like this. So, these are the different levels of the molecule. So, then I also have a very broad band here. So, this is the second layer and this is the third layer of the molecule. So, this is all FePc so that is basically the molecule. And this is the surface. So, now you can see how the electronic structure of the interface changes. So, as you go away from the interface, all that so called interfacial states are basically just vanishing. And then the molecule reach almost to the normal gas phase molecule. And you can also study the evolution of electronics. So, this is also quite important, because if you ever want to actually just use this kind of molecule in technology and to generate kind of interfacial layers, then it is quite important that we need to basically come up with this kind of an understanding of the interface. Good. So that is the example. So, you can see a little bit more details in this particular article. And also, there are many articles available on these kinds of subjects. But these are typical examples, as I told you, you can use them as reference in understanding the electronic structure of the molecular and layers on surface.

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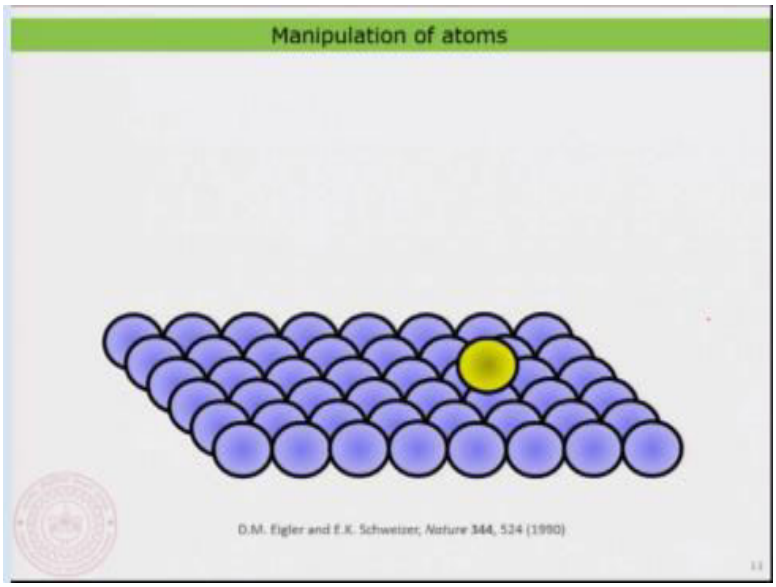

Well, I actually would like to conclude here, because I want to switch now to a new topic called manipulation of atoms. This is actually a new perspective, in fact, new perspective in surface science and also a new perspective of scanning tunneling microscopy. Because this is actually some capability of scanning tunneling microscope that actually is not possible with any other microscopes. So that is the interesting thing, because you have a probe, because you have something in your hand with that you can move things, you actually can manipulate atoms on the surface, you are familiar with this thing, which we have already seen before, I have an adsorbed atom on top of a crystalline surface. And in fact, I can basically just use my tip to move these atoms around. And I can basically create some structures.

I will tell you why we need to create this structure. So, what is the perspective of this structure? It has a lot of futuristic application and also a lot of fundamental interest, as you will see now. Now, what I want to do is actually, I want to move the atom around the surface. And I want to make structures that like I want it. Let us do that. So, I have my tip. And as soon as I bring the tip close to the atom, which is on the surface, so then what actually happens that there is always an atomic force that is acting between the tip and the atom. And therefore, the atom actually also starting to interact with the tip. Of course, to do this, I need to go a little deeper than what I normally do in the imaging case. Of course, in the imaging, I also just stay around 1 to 2 nanometer from the surface. But in this case, I need to really go close to the atom and almost touch the atom. And if I do that, then the atom actually connects to the tip. And then I can drag the atom to a new position. And then finally, I can leave the tip away and the tip would basically just move away and the mole and the atom would actually just go from one position to another position. So, now if I have many, many atoms on the

surface, I can basically just move them around and I can build up structures like I want. So that is the interesting thing about it. So, let us think about making some structures out of it.

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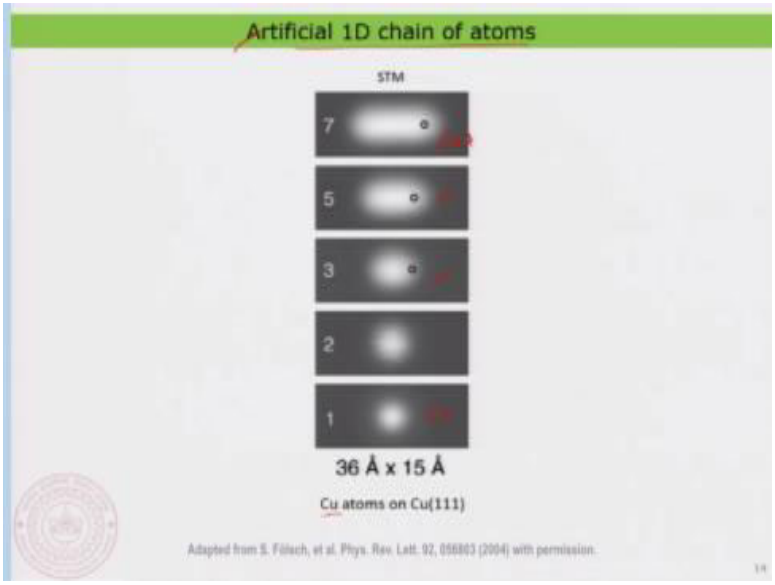

So, what I am going to do is actually, I am going to make something like a 1D chain of atom. So, you will see it in a few minutes. Why I want to do that. So, what I am doing is actually, I would deposit first copper isolated atoms. So, this is for example, a single copper atom sticking on a copper 111 surface. And then after depositing the copper atom, I can basically start to manipulate one atom from one location and bring it close to another atom.

So, I can take one more item and I can start to make a chain of atoms. So, here you can see it is already a copper 7 molecule kind of thing. So, it is, of course, something not naturally existing. And that is why I am calling it as artificial. It is something that you would only create in this kind of system. And of course, you also need a low temperature to do that, because the stability of the atom is very important within this chain. And as soon as you increase the temperature, you would find that these atoms would move around because we have also talked about that normal temperature, they are not stable. But of course if you are a low temperature, you can basically manipulate atoms and then you can put them together and then you can basically create these kind of nice chains. Good. What is the use of this chain? What can we understand from this chain? So, this looks like an artificial 1D chain? Let me recollect something like the first topic of quantum mechanics called the one dimensional box problem. Have you heard about it? I am sure you all have heard about it. And they have also solved the solutions of a one dimensional box problem. Can we think about a one

dimensional box problem using a copper atom chain? Yes, we can. That is what I want to show you.

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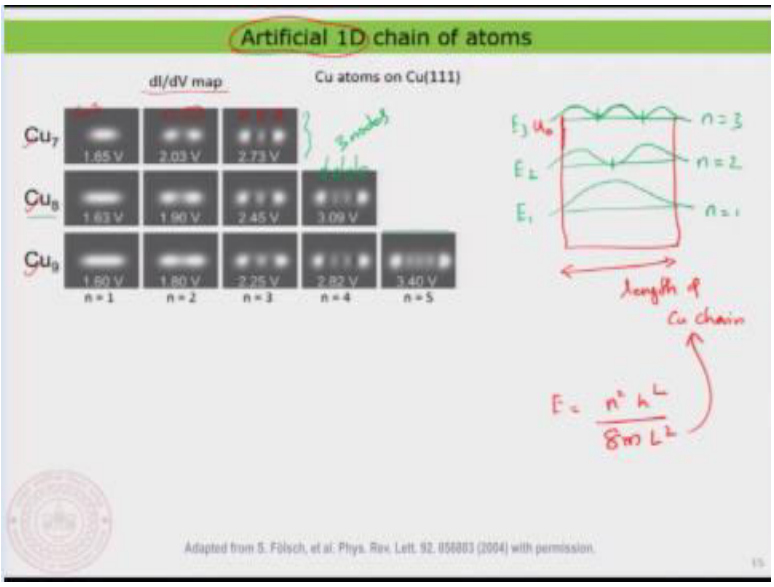

Now, I have a copper chain here. So, I have here a few examples. So, it is a copper 7, a copper 8, a copper 9, 3 different chains, I can make. Any change I want is no problem. So, I can basically just make the copper chain. And then I can image these copper chains at different voltages and make something called a dI by dV map. You will recollect that we can also measure the dI by dV spectrum. And you can also measure the dI by dV at a certain voltage. And you can also image that, which is truly the map of electron density of the molecule or surface or whatever you want to call it. But now something very, very interesting happens, you surely know that this is the copper 7. But when you image them at lower voltage, like 1.6 volts, you see, of course, it appears like a nice long protrusion as expected. But as soon as you increase the voltage to 2.03, you see something spectacular happens that the contrast is actually changing to something like a double contrast that 2 bright protrusions and nothing in the middle. What is that? Well, if you increase the voltage more, you would find again, 3 protrusions are coming. And 2 dots in the middle or 2 dark points in the middle, well, this is not really acceptable. Because you have looked at the copper chain, where I would expect to see a long chain in dependent of the voltage, wait a minute, what we are seeing is nothing but the different electronic levels of the copper atom itself. So, this is what I told you, you can basically consider this as the one dimensional box where the box length is nothing but the length of copper chain that is the length. And then if you would basically have the electrons confine within this particular potential. So, this is, of course, a certain potential, which we can call it as u 0. So that defines something like the height of the

potential well and then you can basically see if I would put basically electrons inside their wave function should basically depend on the energy. And how does it depend? So, you definitely know the solution of it. And the energy, of course, is also depends on the way the quantum number n square h square by 8 m L square, where L is basically the length of the copper chain. And n square is basically representing the quantum number itself. Now, the first electronic state is; I am only plotting the electron density. So, the first electronic state is somewhat like this m and the second electronic state as a wave function that looks like this.

So, this is n is equal to 1 and this is n is equal to 2 and then the third electronic state is basically looking like this. What do you have here? For the n is equal to 2 state, you have 1 node and for an n is equal to 3 state, you have basically 2 nodes. And that is exactly what you are seeing in the dI by dV contrast. So, as the energy increases, of course, this is basically representing the E 1, E 2, E 3 and so on that is basically the energy of the electrons. And that is exactly what you are basically scanning or seeing as you increase the voltage, it is same as also you remember or you recollect what we have seen in the case of molecular orbitals. So, something like that a different state of the copper chain and that is actually equivalent to the confinement of an electron inside a box. So, therefore, the electronic wave functions are basically looking like this with different nodes. And you can see here if I would take basically copper 8, I can go a little bit higher. There, you also see that I have basically 4 lobes that is what I would expect. If I would basically just take n is equal to 4, then I am basically expecting to see 3 nodes here. So, this is what 3 nodes. You can of course, take longer chains. And then you can basically see this nice different electron densities as you would expect to see in a very fundamental quantum mechanical problem. And that is something you can basically now see it in real space. This was never possible before because you also have to create artificial atoms. Without creating artificial atoms, how can you see something like this? Well, to create, you had to discover basically the scanning tunneling microscopy and the scanning tunneling microscopy allows you to move or manipulate atoms. And when you manipulate atoms, you can basically see something spectacular like this. Now, I want to show you a few more interesting example.

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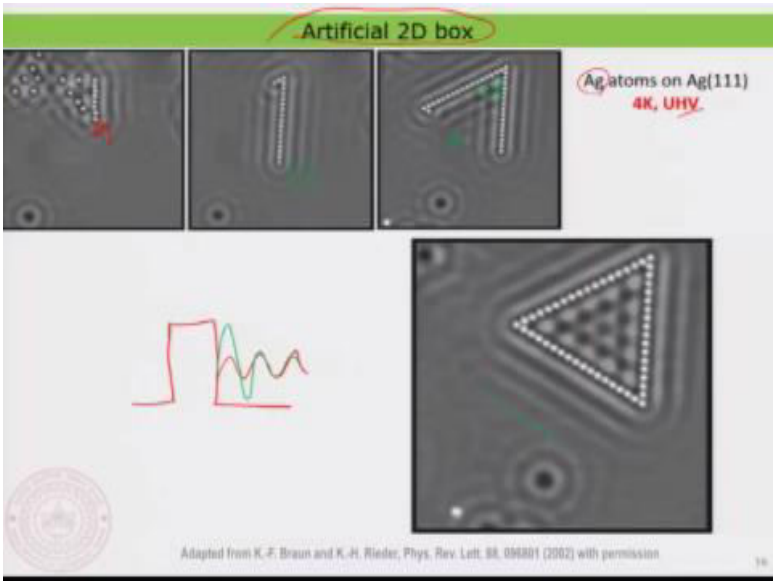

I want to show you also a kind of artificial 2D box. A 2D box means now I am going to create basically, make a chain of atoms and forming a box, basically. So, here, what I am doing is, again, silver atoms on silver surface, again, you can see it all done at very low temperature. And then you can clearly see these are the silver atoms and I am basically manipulating atoms nicely and forming a chain. And you can actually make the chain like this. And you can finally make a kind of triangle a chain. And now when you make a triangle, a chain, what you see something spectacular around the chain is interesting, because everything that we are doing is actually on a 2 dimensional surface, of course, the surface and it is on a metallic surface. What do you expect on a metallic surface is a, (()) **(26:37)** of electrons, in fact. So, the moment you create an atomic grow, is basically that you are creating some kind of a barrier for the electrons that are present on the surface. So that means if there would be an electron that oscillate like this and the moment it comes and see a barrier that means a chain of atom, it would basically kind of reflect, it would basically reflect and then create some kind of a modulating wave that dice out.

And that is also the reason why you see here, there is a ripple of wave, a kind of standing wave that actually reflect from the atomic chain that is actually the electrons that are bombarding the chain of atoms and they basically reflect back. So ideally, what you are visualizing is a standing wave of electron that is created at a barrier. So, this is again a barrier, because this is the atoms that acting as a barrier for the incoming electrons. So, you can now create to have such atomic chains and what you clearly see that these 2 standing waves of electrons start to interfere. You can see now, there is a pattern emerging. On this side, of course, it is, of course, a single wall, the standing wave of the electron comes and

reflect back, no problem. But in this region that is in between, you see there are 2 standing waves that are basically just going in a triangle away, then what happens? They would start to interfere. And finally, when you have the third wall, you can see there is a nice interference pattern within the triangle. And outside, you have this nice standing wave that is actually reflecting back. So, what you are seeing or visualizing is nothing but just a standing wave pattern of the electron interference. Well, that is what you have actually studied. Or that is a reason why you have actually just started studying quantum mechanics because there is a first time you have said, well, to define electron, we need to also understand the wave nature of electron. And that is exactly what you are seeing in this image, you are ideally visualizing the interference of electron waves in a real space image.

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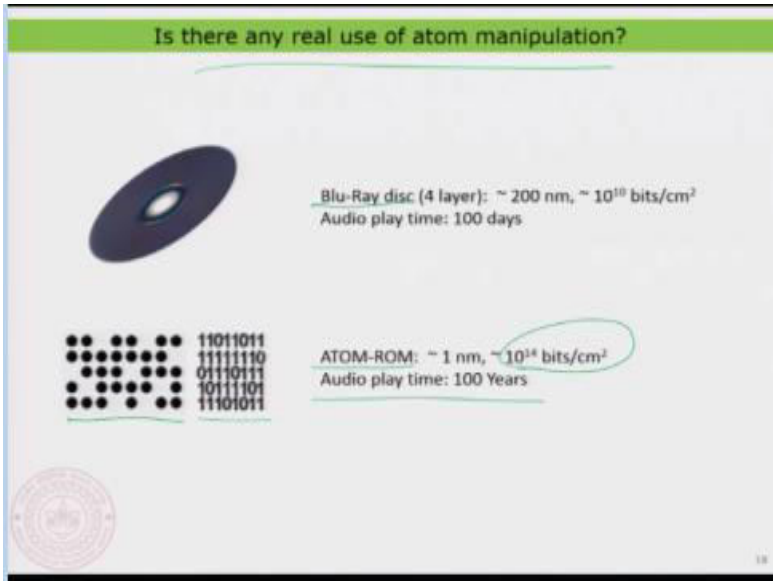

Well, one last perspective that I also want to put, is there anything interesting about manipulating atom in a technological aspect? Yes, there is. If imagine that the information, if you would use the atom as an information with, then I can ideally create an array of atom. And then wherever I have actually manipulated an atom, I can call it as 1. And if absence of an atom, I can call it a 0, therefore, you are ideally creating a row of information, which is something we can call it as atom row. And since, the dimension of the atom row or the bit size is basically just less than 1, the amount of information that you can create within a small space is actually something like 10 raise to 4 times bigger than a typical Blue ray disc. That actually means we can have an audio play for much more than a typical current Blue ray disc. So, this is actually some kind of a future perspective of creating or manipulating atoms on surface, which actually has an interesting perspective.

But it is of course, a little bit futuristic perspective. Well with this, I would like to conclude this lecture and I will see you in the next lecture with a few more interesting aspect of scanning tunneling microscopy. Thank you very much.