

Computational Materials Physics (2023-11-13)

Week 7 : electronic structure

(automated transcription)

This feedback webinar on electronic structure will be a bit different than usual for the ones who used to watch this live. This is not a live stream, this is pre-recorded, because I am traveling right now. And it will also be for other reasons not a standard webinar, because I have a serious jetlag and I feel not very well. Some throat infection or so. So I will try to do my best, but it can be a bit difficult. Well, there was a due date for the project yesterday. So the milestone number 2 had to be submitted, where in the first place the basis set size has to be properly tested and the other convergence tests. I have received all 6 reports, I didn't look at them yet, but I will do this very soon, so the teams can expect feedback on this. But it's nice to see that all teams are still going strong. Then a repetition of something I said before, but because again it came as a question in one of the tasks by one of you, so I repeat it. If you have to use other programs in the virtual machine, like NUPLOT, like XCRISTEN, and you work in the Quantum Espresso environment, they will not be available. And that is because they are installed in a different environment. So therefore keep two terminal windows open, one in which you activate the Quantum Espresso environment, there you do the Quantum Espresso calculations, and one in which you activate the Visualize environment, and there you can use NUPLOT and XCRISTEN. So you don't have to install NUPLOT yourself, that's absolutely not needed. And with this we can come to the scientific topic of this week, so everything related to electronic structure. And this is a point in the course where some people may wonder, yeah now it seems like we are changing gears, and now this is about something totally different. How does that all fit together? So therefore let me emphasize the overall structure. What we did so far, that was if you have an input crystal structure, then you can calculate the total energy. And with that total energy you can search for the equilibrium geometry, and you can find observable properties like the bulk modulus or the equilibrium volume. And you can even predict whether the crystal will exist or not via the phase diagram. So everything based on calculating energies for a given structure. In the present module we add something more. Next to the total energy we will calculate other properties like the band structure or the density of states. And that will allow us to make other conclusions or predictions about the crystal. Is it a metal or an insulator? You could predict from this what is the color of your material. Many spectroscopies that are experimentally performed can be deduced from the electronic structure. We will not do this in this course, but that is definitely possible. So that is where this module fits in the bigger picture. It's new information additionally to the total energy. And in order to formulate things like band structure and density of states, you need to know some language from condensed matter physics. And that is where this reciprocal lattice and quantum numbers and so on were needed for. So I hope that with this the overall storyline is a bit more clear. Reciprocal space, the word was already mentioned. And I gave you a definition of reciprocal space. So you have the direct space where every point represents a position, position vector. With coordinates, reciprocal space, that is the space defined by all inverse coordinates. So a point with coordinates 2, 3 halves will be mapped to 1 over 2, 2 over 3. And I asked you in that respect, if I give you three points, calculate what is the distance between these two points. Well, what is the distance between these two sets? No. What is the distance between the different pairs you can find in these three points in direct space? Then calculate the corresponding points in reciprocal space and calculate the distance again. And what can you conclude about these distances? Are similar distances in direct space corresponding to similar distances in reciprocal space? Well, all of you, as far as I could see, did the right calculations. You found that the distances between the different points are 1. And you could calculate the reciprocal points and you could calculate their distances and you find that they are different from 1. The conclusion that you drew from this is not always the same. Somebody concluded, well, it's still more or less true that similar distances in reciprocal space correspond to similar distances in reciprocal... that similar distances in direct space correspond to similar distances in reciprocal space. Now, that is not at

all true. You can easily find points that... I'm trying to find an example. Let's take two points that have a distance 1 and in direct space. You bring these points very close to the origin. Well, then these points will be mapped in reciprocal space rather far away from the origin. And their distance will be different than if you have the same distance 1 in two points very far from the origin. These points will be mapped very close to the origin and their distance will be almost 0. So you can easily make whatever combinations. There is no relationship or no simple relationship between distances in reciprocal space and in direct space. Having reciprocal space, then we look at the reciprocal lattice. And that is not for everybody easy. And therefore I want to give you a second story that explains the concept of reciprocal lattice... and that distinguishes the reciprocal lattice from reciprocal space in a way how it is not told in the videos. And I think if you have studied the videos and tried to understand them... if you now see this second explanation, then that will make more sense. And for that second explanation I want to go back to something you probably know better than reciprocal space and reciprocal lattice. These are Fourier transforms. And to keep it simple, Fourier transforms in one dimension. So I have a time axis. That's the first of the two axes you see here on this picture. And I have a frequency axis where it's not really the frequency but the angular frequency that is shown here. So not the inverse of the time but 2π times the inverse of the time. Every point on the time axis is mapped to a point on the frequency axis. You can take the point that is at 2 on the time axis. Well that will be mapped to an angular frequency of 2π over 2, so π . Or a point that is 1 on the time axis will be 2π on the frequency axis. Or $1/2$ on the time axis will be 4π on the frequency axis. So every point from the direct space, which is time, is mapped to an inverse time, to a frequency in reciprocal space. So I stress I use the word space here, not lattice. And we have a continuous time axis and a continuous frequency axis. The point with frequency 0, that is mapped to, the point with time 0 is mapped at frequency infinity. So we didn't mention Fourier transforms here yet. I was only describing the two spaces, the two one-dimensional spaces, time and its inverse, frequency, that will play a role in the Fourier transform. Well, let's now take in the direct space on the time axis, let's take a lattice there. What is a lattice on the time axis? It's a series of points in time where something happens. Say that can be a beep whenever the time passes one of these red points. That could be something that is represented by the diagram of the red points on the time axis. Now I take a cosine function and I choose the frequency of that cosine function in such a way that the cosine function is commensurate with this lattice of red points. So that means whenever the cosine function returns to its same, whenever the red point, if you look at any of the red points, the cosine function will get the same value there. So that cosine function is commensurate with the red lattice. And the frequency of that cosine function I put on the frequency axis. But this is not the only cosine function that is commensurate with that lattice. I could double the frequency and it's still true that whenever you are at the red point you have exactly the same value for the cosine function. So the double frequency is also commensurate with this time lattice. And so on for the triple frequency and so on. So you can build a half infinite lattice in frequency and every time you take a cosine function with that frequency it will be commensurate with that time lattice. Now that blue lattice, that would be the reciprocal lattice of the red lattice. And why did you see that in the context of Fourier transforms? Because it has this nice property that any function of the time that has the periodicity of that red lattice. So only the periodicity, it doesn't need to be a cosine function, it can be something totally different. But with the periodicity of the red lattice, well that function can be expressed as a sum over cosine functions with only frequencies that appear on the blue lattice. That's a very useful statement. So that was Fourier transform. The reciprocal lattice for a crystal plays in a way exactly the same role as this reciprocal lattice on the frequency axis. And that is what is explained then in that module on plane waves and the reciprocal lattice. So we use that two dimensional example. If I take a point in reciprocal space where I have a wave vector, so that every point in reciprocal space represents a wave vector which is related to the frequency. Well if I take that wave vector there for the red point, I can draw wave fronts in red where my plane wave in two dimensions reaches the same values. And in general this has nothing to do with the direct lattice. But I can meet some points that are such that every point on the direct lattice that there the plane wave takes the same value. So the plane wave is commensurate with the direct lattice. If that is the case, then the red point, the point in reciprocal space, is here part of the reciprocal lattice. And so we can build a lattice of red points that is the

reciprocal lattice for the lattice of black points at the left hand side. So exactly as my blue points were a reciprocal lattice for the red points in the Fourier transform, are the red points here the reciprocal lattice for the black points in this plane wave construction. With this I asked you to do something. And we were using the kvec tool for the Bilbao server for this. I will come to that part at the end of the exercise. I draw again the attention to using Xcrisden. Some people hesitate, is this on the virtual machine or do I have to do this on my normal computer? So it is available in the virtual machine but with that visualize environment. And so if you are in that environment then with this command you can visualize the unit cell in three dimensions of a quantum espresso input file. So not of a CIF file, Xcrisden cannot visualize CIF files but it can visualize quantum espresso input files. So with CIF to cell you need to go from the CIF file to that quantum espresso input file and then you can visualize it in Xcrisden. In Xcrisden we will display the Wigner Seitz cell of the direct lattice and the Briomann zone. And what was that Wigner Seitz cell or a Briomann zone? If we look at lattices either in direct space or in reciprocal space we can choose a primitive unit cell. There are many possibilities for that. One of the possibilities is given here. But we can also choose that primitive cell in such a way that the lattice point or the reciprocal lattice point is centered at the center of the cell. And if that is the case then we call that unit cell the Wigner Seitz cell for that lattice. And if it is about the reciprocal lattice then you don't use the name Wigner Seitz cell for the reciprocal lattice. You call it the first Briomann zone. Xcrisden can visualize the Wigner Seitz cell for the direct lattice. That is what is shown here. That blue volume is the Wigner Seitz cell for the direct lattice and this is for the iron aluminum example. If you use the tools k-path selection in Xcrisden then you can also do this for the first Briomann zone. This is not for the iron aluminum example but if you would do this for the BCC crystal you would see this picture here. It is even an interactive picture so you can rotate this in Xcrisden and look at the first Briomann zone from all directions. This is a good point to tell something about the conventional and primitive cells. Also for the project this is something that will play a role. I will take the case of BCC. I have here the quantum espresso input file for a BCC cell in what we will call the conventional cell. I have a lattice parameter, something that sets the scale. Then I have my cell parameters matrix. That is here just the unity matrix so it describes a perfect cube. Then I have positions inside the cube given by these atomic positions and with the crystal keyword that is always used by default. That means you have here the positions in fractional coordinates. My first atom is at position 000. But not only at 000 you have to apply periodic boundary conditions. That means you have to draw it also at all other points. My second atom is at position 0.5, 0.5, 0.5. That is inside the unit cell so there is nothing to draw extra due to periodic boundary conditions. That is the conventional cell. But you could now describe exactly the same lattice also with the so called primitive cell. And that cell will be smaller. It has a smaller volume and nevertheless it describes the same lattice. And how is that done? By taking a different choice for the AD and C vectors. So for the three lines of the matrix. For instance I could take minus 1.5, 1.5, plus 1.5. And that is the one you see there blinking. Or I could take 1.5, minus 1.5, plus 1.5. And 1.5, 1.5, 1.5. These are three vectors that together span a unit cell. And if you calculate it you will see that the volume of that unit cell is 1.5 of the volume of the conventional cell. And still it is a unit cell. It is the smallest one you can take but it is a unit cell. So if it is half of the volume there is also half of the atoms inside. And the atoms are here at 0, 0, 0. If you now would make the first brioenzone for a BCC lattice. Then it will depend on will you do this for the conventional cell or for the primitive cell. In both cases you will find different brioenzones. So this here is the brioenzone for the primitive cell. And this is the brioenzone for the conventional cell. So you cannot just look at the brioenzone picture and unambiguously say this comes from this lattice. It depends on which type of unit cell you have taken. These were pictures from xCRISDIN. In the Bilbao server you can find similar pictures. So in the KVEC tool if you look for the BCC structure. Then it will give you for instance this picture. And that is very similar to the one we had from xCRISDIN. It is a bit differently rotated but it is essentially the same picture. And you can even make some interpretations or understand some tables from the Bilbao server that way. So if I take the first brioenzone and I plot them in what is called the conventional basis. So this x, y, z axis here that make angles of 90 degrees. That is our conventional basis. That is the basis for the cube, for the BCC cube. Well my point H, H is just a name for one of these points, a high symmetry point. My point H has coordinates 0, 1, 0. If I take instead the primitive basis. Then you see here B1, B2, B3, the new basis

vectors. They come out of the face centers of this volume. And now my point H has coordinates 1, 0, minus 1, 0, 1, 0. So same point H but the coordinates are expressed in two different basis. This would be the corresponding crystal for the iron-aluminum example. So the first brionzone for the iron-aluminum example is this one here. And about this picture I asked you, take this as a starting point. And can you observe some correlations between the length of the unit cell in direct space. And the length of the brionzone in the same direction in reciprocal space. There was one very short answer, they vary inversely. The longer answers show a bit better why this happens. So you have, if you follow the general equations. You find that the length of lattice vector A in the reciprocal space. Is inversely proportional to the length of the lattice vector A itself. And that is illustrated here on this picture. Where I took the iron-aluminum example but I exaggerated this a bit. So I took a distance of 1 in units of A in the x-direction, 2 in the z-direction and 4 in the z-direction. And if I calculate for this with x-grids then the reciprocal, the first brionzone. Then you see this. And the x-direction which was the shortest direction in direct space is now the longest one. And the z-direction which was the longest direction in direct space is now the shortest one. So it's really this inverse relationship. You can see that from the expressions. So here you had them in 2 dimensions. These are the expressions in 3 dimensions. And you can just mathematically inspect that that inverse relationship is there. Let's bring that back to our example of the Fourier transform. Here we had a lattice on the time axis and a reciprocal lattice on the frequency axis. Now I take a lattice on the time axis where the lattice vector, the single lattice vector in 1 dimension is larger. So something like this. The corresponding reciprocal lattice will be smaller. And if on the other hand we take a time lattice that is more condensed, that has a shorter lattice vector, then the corresponding reciprocal lattice will have larger dimensions. So you have a 1 to 1 relationship there. Then we come to the topic of plotting wave functions and densities. And that is very much related to the concept of quantum numbers in a crystal. So I gave you the O₂ molecule. And I asked you how many quantum numbers would you need to label the many body wave function of this entire molecule. And do this once with and once without the Born-Oppenheimer approximation. This gave quite some numbers as a result. So this is an overview of all the different numbers I got. Some very small, some rather large. What are the right ones? Well, the ones that are indicated in red here. 64 for the situation with the Born-Oppenheimer approximation. And 70 or 72 without. How do you find that? Maybe first this. In the video I said that the O₂ molecule has 8 degrees of freedom at a given time. So that was a lapsus. That is absolutely not true. Totally wrong. Please correct that. So how do we find the correct answers on the previous question? Well, this is the way how you can count. In the O₂ molecule you have 16 electrons. Every electron has 4 degrees of freedom. 3 spatial one and 1 spin degree of freedom. So 16 times 4. Definitely you have 64 quantum numbers for the O₂ molecule with the Born-Oppenheimer approximation. Without the Born-Oppenheimer approximation it can depend a bit. Either you say we have now 2 nuclei together with our 16 electrons. Nuclei 2 can move in space, so 3 degrees of freedom. And they can have a spin, so an extra degree of freedom. So that's together 16 plus 2 times 4 degrees of freedom. That's 72. Or you can say a nucleus, well we will not consider this as a quantum particle. It will have no spin. I'm losing my line of thought here. So if the nucleus is considered not to have spin, but is just a picture with spatial degrees of freedom. That is what I wanted to say. Then we have not 4 degrees of freedom, but 3 degrees of freedom for the 2 nuclei. So rather than 8 extra quantum numbers it would be only 6 extra quantum numbers. It depends a bit on how precise you want to do it. Whether you want to have this spin for the nucleus included or not. There was somebody who did a different reasoning for the 6 degrees of freedom for the nucleus. That was tiered apart in 3 translations. 2 rotations and 1 vibration. And that's perfect. That is another way to represent these 6 degrees of freedom. But this is not so easy to generalize for 3 nuclei or 5 nuclei. Which translations and rotations and vibrations are still allowed there. That's not so easy to find. So the way of counting by just looking at the number of particles and multiply it by 3 or 4. That is much faster if you just want to know the degrees of freedom. I said it depends on how precise you want to be. Whether or not you consider the spin of the nucleus. Some people may even wonder why does a nucleus have spin. Well it's different than for the electron spin. All electrons have the same spin. It's a property of the electron as a point particle. But nuclei are not point particles. They are composite particles made from many different protons and neutrons. So you will need to construct the spin based

on the number of particles that are included. But the result is that there will be some spin for the nucleus. Not a value that you can just predict. It has to be measured. But every nucleus, every isotope can have a particular value for its spin. If you want to learn more about this. About how the role of spins of the nucleus can effect measurable properties. Then I can recommend to you a course on hyperfine interactions. That's a course in the second term at Ghent University. That is run in exactly the same way as this computational materials physics course. But for a totally different topic. For hyperfine interactions. And we explore there first the physics of hyperfine interactions. And then we look at experimental methods that are based on hyperfine interactions. So this is just as an aside for those who may be interested in this. Now having our quantum numbers. How can we use that to plot wave functions and densities. And these are one particle orbitals you see here. But let me emphasize what is the difference between one particle orbitals. And the total wave function of the total density for which we need the entire set of quantum numbers. So it's generally true that every state of a system. Every configuration of a system. That this is labeled by a set of quantum numbers. So for the many body wave function of an atom or a crystal. You need to take an object with as many variables as there are. You need an object that can be labeled with as many numbers as there are degrees of freedom in that system. That's the second statement here. And if I apply this to the hydrogen atom. Where in the Born-Oppenheimer approximation you have only one particle the electron. So that means four degrees of freedom. So we have indeed four quantum numbers that correspond to that. Well this is a situation with a one particle. And it will often be insightful to project that many body wave function. Into such simpler one particle contributions. Which one particle contributions can we recognize in the full many body wave function. So therefore one particle contributions like the ones you see here indicated. If this would be say a uranium nucleus. Well what is a 1s electron? That is a concept from hydrogen. But you are talking about a uranium atom. How does that fit together? Well you take the uranium wave function, uranium many body wave function. And you look to what extent you recognize in that wave function the 1s electron. So this is why one particle orbitals are often drawn. Even though in principle you have to consider the many body wave function. I told this for the uranium atom. For a crystal that will be equally true. We will also there be able to draw one particle orbitals. That are labeled by just four quantum numbers. And next week we will see explicit examples of that. In order to help you to get a feeling for thinking about this. I asked you to inspect some pictures in detail. For in this case the 2p orbitals in hydrogen. And that was not for everybody that simple. So let me emphasize that you have here different solutions for the 2p wave function. Than for the 2p density. Wave functions can have signs that are different from positive. While the density. I feel my thoughts wandering away. This fever and jet lag is really not helpful. What was I saying? You have different signs in the wave function. They can be positive and negative. And that is what is labeled here by colors. The densities are always positive. But you still see the colors that refer to the underlying sign of the wave function. And by playing with these isosurfaces. Where do you cut this picture to draw these isosurfaces. Depending on that you get connected or disconnected spheres. So you can really try to understand this visualization. If that doesn't succeed it is not too important. It is helpful to be able to do so. But it is not something where the rest of the course depends on. With quantum numbers for a crystal. How do we use these to label the wave function? What are the quantum numbers that label the wave function for a crystal? Well first we have to examine how many degrees of freedom we have. And that is relevant for a macroscopic piece of material. So I take a block of crystal. And I count how many unit cells do I have in that crystal. And per unit cell how many electrons do I have. So if we call n the number of unit cells and m the number of electrons. Then n times m is the total number of electrons in the macroscopic piece of crystal. And times 4 is then the total number of degrees of freedom. 4 times m times n . Where do we find 4 times m times n quantum numbers? Because that is an enormous number. That can be found in the following way. You take the first Brillouin zone. And in the first Brillouin zone you take n different points. Not randomly according to a certain algorithm. But n is very large. That is the number of unit cells in a macroscopic piece of matter. So that is really a huge number. So therefore these points are almost continuously taken. It is discrete but it is almost continuous. So 3 points in the first Brillouin zone. Every point is a vector with 3 components. So these are 3 times n independent values. They could serve as 3 times n quantum numbers. But on top of that for every point in the first Brillouin zone. For every such

position point we can have on average n different bands. One band per electron. Because the bands are filled by the number of electrons. So for one unit cell we should fill n bands. So if we take the band index as a quantum number. Then we have 3 times n times n . And we can take the spin as well. So we have 4 times n times n quantum numbers. So specified by a vector in the first Brillouin zone and a band index. That is a huge amount of quantum numbers. And visualizing that is not so easy. And therefore we saw 2 ways how to do that. You can take a linear path through the first Brillouin zone. And plot all eigenvalues along that path. That is how you get the band structure. Or you can project everything on an energy axis. And that is how you get the density of states. Both are incomplete ways to represent that entire amount of information. But at least they keep some relevant features of this. And we looked at this. Was this for the aluminum crystal? I forgot. Somebody made a few years ago the remark that these graphs are almost textbook ready. And that is indeed true. Until say 10-20 years ago. Having band structures in a textbook that was a very precious thing. Band structures were calculated only for very few crystals. Takes a lot of work if you have to do that without a computer. But nowadays band structures can so easily be obtained out of DFT codes. That these pictures are totally easy to get now. And you can recognize in such pictures like in this one. You can recognize there the cartoon information that you have in many textbooks. The valence band, the conduction band. And in this case the gap between them. And there are many pictures that you can google where similar ideas are presented. But you have to realize that these are cartoons. And that now you are able to calculate the real thing. And for the crystal here and that was FCC aluminum. For FCC aluminum I asked you to look at this series. Where you have FCC aluminum with the equilibrium lattice parameter on the left hand side. And three artificially expanded lattice parameters. Why do these bands get flatter if you increase the lattice parameter? And why does the 3s band get flat before the 3p band? And that one again before the 4s band and so on. I have to point out a misconception here. One of the answers told something like this. For an infinitely large lattice parameter the electrons would behave like free particles. And therefore the energy levels would become continuous. That is not what is happening here. In this exercise I am not bringing the electrons farther away from each other. I am bringing the atoms farther away from each other. So you increase the lattice parameter. The distance between the atoms becomes larger. But the electrons they remain at their atom. It is not that you have some homogeneous electron gas with vanishing density. Because the lattice parameter of the electron gas would be too large. So no that will not happen. What does happen? Well you have atoms that are increasingly farther away. So that are increasingly more like free atoms. And once you have a free atom. Every electron in a free atom behaves the same. Once you have described the energy levels of one free atom. The other free atom of the same element should be exactly the same. So the structure, the dispersion in these bands. That is necessary for crystals. That dispersion gradually disappears. If you get more towards a collection of free atoms. That is the observation or message. And why does the 3s flatten faster than the 3p? That is given here in this answer. The 3s is more closely bound to the nucleus. The 3p are more to the outside of the atom. So the 3p will feel the effect of the neighboring atoms still longer than the 3s will feel them. And this is here an answer that describes more technically how that is possible. So if you bring the lattice parameter to infinity. Then your first Brillouin zone shrinks to a point. And if you then sample that point. If you then put all the quantum numbers on that same point. That will be the same point. So the energies you have at every quantum number will be the same. So that is the technical way how you can see. That if you describe a solid by an enormous supercell. That the picture remains consistent. This has brought us to what will be the topic of next week. And next week we will consider chemical bonding. So a more chemistry oriented topic. We will classify chemical bonding in a very simple way. A naive textbook way. But that will be sufficient to be able to tell again some more things about crystals. To predict a few more properties. I just flash here the link where you can put your summary of the past week. And formulate an exam question. I will not let this run during 5 minutes as this is pre-recorded. And I will also not be able to ask for were there any additional questions. I looked in the forums and questions that were asked have been answered throughout the webinar. But as this is pre-recorded I cannot probe for your live questions. So with this we can finish this. It was not easy to make this webinar. But it succeeded. And next week will indeed be different. Because I will not yet be back from that conference. I will arrive that same day. So also for next week I will have to pre-record this. Not yet

sure how exactly that will happen. Because I will be traveling over the weekend. But we will find a way. Okay. Then we finish here. And we will see each other back pre-recorded again next week. With the topic of chemical bonding. Bye bye.