

## Computational Materials Physics (2024)

### *webinar 07 – electronic structure*

This feedback webinar on electronic structure was planned to be a live webinar, but I didn't take one thing into account, and that is that it would be a holiday in Belgium on the scheduled day, so therefore I made a pre-recording on Sunday evening, after having read your reports, and this is once again not a live webinar. Should you have specific questions about the past module, then you can still put it either in Zulip or in the forum. Questions that were on Zulip, I have already answered on Zulip itself. There were no additional questions in the forum, but should there be, please send them that way, and... Then it will hopefully not be too much of a problem that this was not a live session. It will be streamed at exactly one o'clock local time on YouTube, as usual, for the people who do not want to interrupt their weekly routine, and it will be from Sunday evening probably, or Monday morning on the course website. Before we start with the science, I would like to remind you of something about the project. So there was a bit of confusion, and that's my fault, about when the second milestone about the convergence testing would be due. In the general overview with due dates, it was set for this week, but in the module schedule it was planned only for next week, and this is because there was some inconsistency. Somebody pointed me to that a few weeks ago. I tried to make everything consistent, and it is as far as the course modules are concerned, but the old due date was still in the list of important dates. Well, never mind, I will give feedback on the ones who submitted, for... who submitted this weekend, and if you did not yet submit, then it's okay to have one extra week of time for that. Then some other announcements and housekeeping things. There was a problem for some of you with using GNUplot and x-christen in the virtual machine, and that is because, well, since last year already, the virtual machine requires to activate the visualize environment, before these programs are available. So in the terminal where you use GNUplot or x-christen, you have to type this `conda activate visualize` command first. I had modified the instructions to include that, but somehow these modified files did not make sense. This is changed now, so now you have the proper instructions immediately within the task, how to do that. My apologies for those of you who struggled for too long with that. I saw some comments about it in the are you on board forum, so apologies. Another thing I noticed, there was one quiz answer that ended with the statement that you see here on the screen. This is a direct copy-paste from that answer, so I guess you know what it means, just as I know what it means. And I can only repeat once again, you don't do yourself a favor if you use ChatGPT or whatever to solve, the questions for you. It is meant to make you thinking about this content, and to make you think already early in the term, long before the exam. If you do that, you really will benefit from that. If you don't do it, well, it's in the first place not helpful for yourself, it gives useless work for me, because I have to read these things, and well, it's by far not interesting for me to read what ChatGPT has written as an answer. I want to know your answers, and I want to spend time to your answers, but not to the answers of a computer code. So please don't do that. It doesn't help anybody. I know I will have to change, the setup of this course, because it was made in a time when these tools were not available. So I will have to find alternative ways, alternative questions, or alternative ways to collect answers, where this is prevented. But I'm not yet there. I'm thinking and searching. And with that we can come to the science. Electronic science. Electronic structure was the topic of this week. And it happens quite often, not this year, but it happens quite often, that people get a bit lost at this stage of the course. And therefore this is a good moment to look back, and to emphasize the overall structure. So until before this week, what did we do? Basically one thing, we learned if you give a specific unit cell to a DFT code, meaning you determine the volume, the shape of the unit cell, and the positions of the atoms within the unit cell, then the DFT code can calculate for you the total energy. We have seen what the physical meaning of that total energy is. And by knowing the total energy, and then playing with the volume and the shape, and everything, we can find the equilibrium geometry of that crystal, we can find an elastic modulus like the bulk modulus, we can even prove whether or not that crystal can exist

in nature by constructing the phase diagram. All of that is based on total energy only, and specifying details of the crystal structure. That is a lot of information that is already available this way, but it's not every piece of information that you could imagine about a crystal. You could for instance ask questions like is this crystal a metal or an insulator? Which color would it have? Or you could do one of the many spectroscopy methods that exist in experimental physics, and wonder how would the result of that spectroscopy experiment be? What would be the prediction of the result of that experiment? Such questions cannot be answered based on the total energy. But it can be answered based on the thing which we call the electronic structure, visualized as either the band structure or the density of states. That's a topic. Typically from condensed matter physics. And that was the topic of the past week. We will see in the coming weeks that there are also topics that are more specific for chemistry, more specific for materials engineering. Each of these fields will have their week, their module, but the past week was the week of condensed matter physics terminology. And the first concept there was the concept of reciprocal space, which, quick reminder, we defined as a space where all the coordinates of the points are the inverted coordinates of the points in real space, in direct space. And we always gave these two-dimensional representations. Of course, in general, we do this in three dimensions. But this is something easier to think about. I ask you to consider the following question. You get two points, or three points, with their coordinates in 2D space. In 2D space, you calculate the distance between the points, and then you determine the corresponding three points in reciprocal space. Find the distance, and consider the questions. If two points lie at similar distances in real space, will they be at similar distances in reciprocal space? And I give here two answers that were in your reports. So the points, you can read later if you want, or you can post the video to read. The answer in text, I will look at the answer in the bottom in numbers. The points A and B were at the distance 1 in real space. B and C were at the same distance 1. But in reciprocal space, the distances between these two sets of points were not equal to each other. So clearly, reciprocal space does not conserve the distances between points. It's... It's even worse, it totally warps the distances. All points that are very far away from the origin in direct space will be mapped very near to the origin in reciprocal space. So distances far away from the origin will become almost zero. We will use reciprocal space to construct the distance between points. And we will construct something that is called the reciprocal lattice. And if you haven't had courses on condensed matter physics before, then I know that this is not an easy concept. Therefore, I will spend a few minutes of this feedback webinar to tell part of the story that was in the videos again, but in a slightly different way. And hopefully that will give those of you who need additional insight, probably this will... Hopefully this will help you. And I will do that by looking at a situation that you know very well from a different context. Not space, but time. Let's consider a one-dimensional time axis with an origin and the point that indicates one second. And now... Now I take something, yeah, a frequency axis. Where the, yeah, and I have it, okay, and I have a transformation as indicated here on the slide, that the circular frequency  $\omega$  is found by dividing  $2\pi$  by the time. And in this way I can map every point from the time axis to that circular frequency  $\omega$ . And in this way I can map every point from the time axis to that circular frequency  $\omega$ . And in this way I can map every point from the time axis to that circular frequency  $\omega$ . For instance the point that would be at time 2 would be on the frequency axis at  $2\pi$  over 2, at  $\pi$ . That is the point that you have indicated there. Time one would be mapped to  $2\pi$ , time one half would be mapped to  $4\pi$  and so on. Time one half would be mapped to  $4\pi$  and so on. So just as direct space is equal to this point, So just as direct space is equal to this point, space is mapped to a point in reciprocal space, every point on the time axis is mapped to a point on the frequency axis. Points that are very close to the origin on the time axis will be mapped to almost infinity on the frequency axis. I will be working towards a one-dimensional Fourier transform, but at this stage we don't have a Fourier transform yet, we just have two axes, two spaces, just as we had direct space and reciprocal space. Good, now we take on the time axis a lattice, just as we had a lattice on the direct space. That time lattice, you can imagine this as a number of beeps, so time proceeds, and every time when we hit one of these red dots, there is a beep. I could try to transform this time lattice to points on the reciprocal time axis,

on the frequency axis. But as you remember from the previous diagrams, this would just bring all points that are close to the origin on the time axis far away on the frequency axis, and the farther away you are on the time axis, you would get closer to zero on the frequency axis. So this would not be a regular set of points. We can do, however, something differently. I draw now. A cosine function that is chosen in such a way that it is commensurate with the time lattice. And that commensurate means, at every point on the time lattice, on every red dot, my cosine function reaches the same value. That cosine function has a frequency, and I can mark with the blue dot that frequency axis is at every point on the time axis. This is not the only cosine, however, that is commensurate with the time lattice. I can take this cosine function, with twice the frequency, and this one still has the property for every point on the time lattice it reaches the same value. There are other points on the time axis where it reaches the same value. But I do not have all the cosine functions. reaches the same value, but we don't look at that, we are happy to note that for every point on the time lattice it reaches the same value. Therefore also the double frequency can be marked on the frequency axis by the second blue dot as a frequency that leads to something, to a function that is commensurate with the time lattice. And with three times the frequency we have this as well, and we can extend that to infinity, we can have an infinite set of frequencies that all lead to cosine functions that are commensurate with the time lattice. And now we are very close to the concept of a Fourier transform, I will not explain those details, but I'm sure you remember the property that any function on the time axis, however complex it looks like, any function that has the periodicity of that red time lattice, that can be expressed as a sum of cosine functions with frequencies that are exclusively belonging to the blue frequency lattice. So you can forget any other frequency, you just need the frequencies on the blue lattice, and you can construct any periodic function that is commensurate with the red lattice. That is the idea of a Fourier transform. A continuous periodic function is represented by an infinite but discrete set of frequencies. And this is so. And this is so. And this is so. This is something that is now very similar to what happened with the reciprocal lattice and plane waves. So now I go back to what we had in the video, we had our direct space with a direct lattice that represents a crystal. We build reciprocal space, where every point has inverse coordinates. every point in reciprocal space can represent a wave vector for a wave that you can draw in direct space and the planes that have where the wave reaches the same values, these are the red lines that are drawn here on the picture, these planes are perpendicular to the wave vector and they have a periodicity that is determined by the length of the wave vector. Good, you can now search for particular plane waves that are commensurate with the direct lattice and I have here an example if you take the wave vector that is at  $\pi/2$  you have this particular plane wave that indeed reaches the same function value. for every point of the direct lattice and we represent that on a somewhat easier axis system so I now take  $\pi$  as unit and so indeed the point  $\pi/2$  this one here is a point on the direct lattice all other red points at the right-hand side will lead to wave vectors that will lead to plane waves that are commensurate with the black points at the left-hand side. So just as we did with the blue frequency points here the red reciprocal lattice points they form a lattice in reciprocal space that gives you wave vectors for waves plane waves that are commensurate with the original lattice in direct space. And it's on this concept that you now made some exercises. I will deal with the first part of that exercise soon. I will first have an elaboration on another aspect. So what will we do? We will use the Bilbao crystallographic server where there is a tool called Kevec where we can inspect the first Brion-Wein zone. We will come to it what that means for a given crystal. But first I will look at X-chrysdn and at Wigner-Seitz cells and a tool to find a path in the Wigner-Seitz cell or the first Brion-Wein zone. You can install X-chrysdn on your laptop even if that is a Windows laptop that is possible maybe not straightforward but you don't need necessarily to do that because you can also call X-chrysdn from within the virtual machine provided you have once again that conda activate visualize statement. So if you do that and you then take a quantum espresso input file not a SIF file X-chrysdn cannot visualize SIF files directly but a quantum espresso input file then with the command X-chrysdn double hyphen pw underscore input and then the name of your input file you can visualize the crystal structure that corresponds to that input file. Within X-chrysdn you

can rather easily display Wigner-Seitz cells for the direct lattice or Wigner-Seitz cells for the reciprocal lattice which are then called Brion-Wein zones. We had said that in general in one of the videos you see here a picture of two primitive cells one for the direct lattice one for the reciprocal lattice a primitive cell that is a primitive cell. contains one lattice point, but there is a particular choice of a primitive cell possible, there are infinite choices possible, but one of them that is constructed in a specific geometric way, where the lattice point is, yeah, loosely spoken, very much in the center of that primitive cell, such cells are called the Wigner-Seitz cell of that lattice, and if you take the Wigner-Seitz cell of the reciprocal lattice, then this one is called the first Brion zone. In X-CRIS then, if you take the display menu and their Wigner-Seitz cell, and then for this is an example here for our iron-aluminum crystal with its orthorhombic unit, unit cell, you can visualize the Wigner-Seitz cell of that direct lattice. If you take the tools in X-CRIS then, and then k-part selection, then you can visualize the first Brion zone. And here, yeah, there is some hesitation possible, because you can visualize both direct lattice, and reciprocal lattices, either as a primitive or as a conventional cell, and for some lattices, this can make a visual difference. I'm not sure whether X-CRIS then always smoothly makes this distinction with quantum espresso input files. That could be that this is not the case, but in any case, this is a good place to make another short elaboration, and to draw your attention to the meaning of primitive versus conventional cells. Keep the picture here at the bottom right in mind, we will come to that in a few slides. I will first go to an example of a crystal where you do have a difference between the conventional unit cell and the primitive unit cell. And that, that example crystal is our very familiar and common BCC iron. You see at the left hand side, an input file for BCC iron. I specify a lattice parameter. I have a matrix where, remember, the first line, these are the three coordinates components of the A lattice vector. This obviously determines a cube. And in that cube, we have a few atoms. I put here at the right hand side a snapshot from the quantum espresso keywords website, where you can see how the coordinates that are given here are defined. And you see there is an iron atom at position zero zero zero. That's this green point. And because of periodic boundary conditions, that point appears at all other corners of the cube. And then there is a point one half one half one half, the orange point that is in the body center. So that is what this conventional unit cell for BCC iron means. However, that unit cell is not the smallest possible unit cell. It is not a primitive unit cell. You can make a unit cell that still represents the BCC lattice, but that is smaller. And that happens in this way. I can define this in this way in quantum espresso. I still take the same unit of distance, but now my A lattice vector has coordinates minus one half plus one half plus one half, so if I start from the origin, minus one half in the x-direction, plus one half in the y-direction and plus one half in the z-direction, I get here at this body centered atom. The second coordinate, one half minus one half one half, goes here. The third one goes here. And this is a unit cell in which there is only one iron atom present at the corners of that unit cell. And if I visualize that, it would look like this. The green points here, the blinking green points, these are the four green points that are also in this diagram. So this is a cell with only one atom in the unit cell, and it perfectly describes the BCC lattice. Well, why do we need that in this context of electronic structure? I told you this is an elaboration, because it has an impact on the visualization of the brionzone. If you take the primitive unit cell and you visualize in x-chrysthen the corresponding brionzone, then you will get this object at the right hand side. If you take the conventional unit cell and you visualize the brionzone, you will get a cube. So how the brionzone looks like, that really depends on how your unit cell is defined. If you are not aware of that, you can run into a lot of interpretation problems. Well, let's work for a while with the primitive unit cell. We have this, we then have this brionzone in x-chrysthen, and that is also the brionzone that you will see in the KVEC tool of the Bilbao crystallographic server. So if I go back and forth, you may need to rotate these pictures a bit. But, these are exactly the same shapes. Now, in the Bilbao crystallographic server, you also have some, well, you have the first the definition of some special points in the first brionzone, names of special points, and you have tables with coordinates of these points. For instance, the point H has coordinates 0, 1, 0. And I see this on this axis system. There is the k-x-axis that comes out of the screen here. That point H has coordinates 0 on the k-x-axis, coordinate 1 on the k-y-axis, and 0

on the k-z-axis. So, indeed, 0, 1, 0. But there is also an alternative, alternative set of coordinates in the primitive basis. And there is another picture there, in the paper of Setiawan and Curtarolo, to which we referred in the videos. Here you see that there is not a k-x, k-y, k-z, but  $b_1$ ,  $b_2$ ,  $b_3$  basis vectors, that point in different directions, and that point H is at these coordinates. in that primitive basis. So, depending on which basis you take, you can have different coordinates for these points. So, you need to know in which basis do you work, and depending on whether you started from the primitive or the conventional cell, your brionzones may look even differently. Well, all of this is a long elaboration to come to the final conclusion on our iron and aluminum example. What is there the first brionzone? It is an orthorhombic crystal, so we can't hesitate between primitive or conventional. There is no conventional choice possible for an orthorhombic crystal, so uniquely this is the picture from the Bilbao server for the first brion zone of that iron aluminum crystal. I asked you about and this was then using the KVEC tool of the Bilbao server to show the first brion zone and the special K points of that iron aluminum crystal and the special K points they are here indicated with these capital red letters. I also asked which relation do you observe between the length of the unit cell in direct space and the length of the brion zone along the corresponding direction in reciprocal space. And here are a few of your answers the first two above the red line are definitely correct. If the length of my unit cell in real space is A, I observe that the length in reciprocal space is  $2\pi/A$ . So the larger A is, the shorter the length will be in reciprocal space. That second answer has the same but with a bit more numerical detail. The third answer here is I don't think it's right because here you see reciprocal length is proportional to the real length. That cannot be true. How does that look like for real? I have now taken my orthorhombic unit cell but I have for visualization purposes exaggerated how it looks like. So I take my B lattice vector twice. As large as the C lattice vector, as the A lattice vector and the C lattice vector even four times as large. So very strongly orthorhombic. This is how such an orthorhombic cell then would look like in X-chrysdyn, direct space. I make the first brion zone out of this and you see as expected this orthorhombic volume. But you also see that if I go along the shortest direction in real space, so the X-direction, the A-edge is the shortest one. Well that is the longest direction in reciprocal space. A-star is along the longest direction. And the longest in real space, the C-direction, the Z, that's the shortest in reciprocal space. So indeed this inverse relationship. We had given some expressions for this in the video in two dimensions and if you would look in Wikipedia you would see the equivalent expressions in three dimensions. And this is again very similar to what has happened in our Fourier transform, in our relation between time space and frequency space. Because, well, I had a time lattice in red corresponding to a frequency lattice in blue. I could define some time lattice parameter which is the distance between two red points and a frequency lattice parameter which is the distance between two blue points. And remember we had an inverse relationship. So what happens if I make the time lattice parameter larger? If I increase the distance between the red points, then the distance between the blue points decreases. And if I decrease the distance between the red points, then the distance between the blue points increases. You can very explicitly verify that for yourself by thinking again about these commensurate cosine functions and then you will be able to convince yourself that this inverse relationship is really true. After the reciprocal lattice we come to the last important concept of this week and that is quantum numbers. And how they relate to wave functions. First I gave you a very simple molecule, the O<sub>2</sub> molecule, and I asked you how many quantum numbers do you need to label the many body wave function of the entire molecule. And answer this with and without the Born-Oppenheimer approximation. What did you answer? This is a collection of the numbers I received with the Born-Oppenheimer approximation. The numbers ranged from 2 to 96, without the Born-Oppenheimer approximation from 8 to 102. What are the correct answers? 64 with the Born-Oppenheimer approximation, and depending on how you reason, 64 with the Born-Oppenheimer approximation, and depending on how you reason, 70 or 72 without the Born-Oppenheimer approximation. How do we find these numbers? First I should add here, in that video I said something totally stupid at 4.04, the number of degrees of freedom of the O<sub>2</sub> molecule. So that was totally wrong and I really should redo that video, but I forget it every year. I

think this is the third year in a row that I have to point you to that mistake. So how do we find these numbers? There is no discussion with the Born-Oppenheimer approximation. You have no impact from the nuclei, they are at fixed positions. So you only have twice 8 electrons, so 16 electrons. And every electron has 3 spaces. So you only have 2 spatial degrees of freedom and 1 spin degree of freedom. So 4 degrees of freedom in total. 4 times 16, you need 64 quantum numbers to specify the state of the O<sub>2</sub> molecule with the Born-Oppenheimer approximation. If you do not consider the Born-Oppenheimer approximation, then you can say, well I have 2 nuclei, each nucleus has 4 degrees of freedom, position and spin. So that's 8 extra quantum numbers, so that brings our total to 72. Or, if you consider the effect of the spin of the nucleus as being negligibly small, then you can say, my 2 nuclei, they have just 3 degrees of freedom, spatial degrees of freedom, and we have only 6 extra quantum numbers. So a total of 70. You can also reason even in a different way to find the same result, but in a totally different way of thinking. You could say, O<sub>2</sub> molecule, 2 nuclei, how can I characterize the spatial degrees of freedom of these 2 nuclei? I can say, there are 3 independent ways to translate this collection of 2 nuclei. They can also rotate about 2 mutually perpendicular axes, and they can vibrate, the 2 nuclei can oscillate with respect to each other. 3 plus 2 plus 1, that's 6, so this is an alternative way to represent these 6 spatial degrees of freedom for 2 particles. However, although that is very insightful for 2 particles, it rapidly becomes very very complicated for more than 2 particles, so it's much easier to count the quantum numbers just with 3 spatial degrees of freedom per particle. A few years ago, somebody turned out to be very much surprised that this 4th degree of freedom for a nucleus, the spin degree of freedom, that that was present. And, well, yes, if you have had a course on nuclear physics, you will know that nuclei do have spin, and I can use this even as an occasion for an advertisement. I have another course at Ghent University that examines exactly that, how the spin of a nucleus can lead to measurable properties in solid state physics. There is a whole class of experimental methods, hyperfine interaction methods, that are sensitive to that, and you can use the spin of nuclei and other properties of nuclei to learn something about either the nucleus or the crystal in which that nucleus is embedded. So, should you be interested in that topic, feel free to look at [www.hyperfinecourse.org](http://www.hyperfinecourse.org) and you will find a course very similar to the one you are currently taking, but about a totally different topic. And, that same person that wondered why do nuclei have spin, also wondered why do you consider the entire nucleus and not the protons and neutrons from which it is built. And that is a matter of energy scales. It turns out that nature is kind of kind to us, and that is why the protons and neutrons in the nucleus are so strongly bound that it makes sense to first work out what happens in the nucleus, and once you have found the nuclear state, then you can go to the next level and add electrons to this. Strictly spoken, you shouldn't do that. The nucleus is a quantum problem, where protons and neutrons interact and they settle into a ground state, determined by the properties of these individual quantum particles. And then you add electrons to that, which is another set of quantum particles, and you should consider the entire collection. So, neutrons, protons, electrons that are interacting with each other with the coulomb force, with the strong force, and do the quantum calculation for that entire zoo. But because the interaction between protons and neutrons is so much stronger than the interaction between protons and electrons, we can do it in two steps. We first work out the nucleus, and only when the nucleus is done then we take that for granted and we add the electrons. So, strictly spoken, this person who made that remark was right, you should split this in individual particles, but because the energy scales are very very different, we can get away by cutting the problem in two. If that would not have been possible, then there would not have been a distinction between nuclear physics and solid state physics, or atomic physics, for that matter, then you would have then you would need to take everything as one inseparable problem. Good, we realize that we need quantum numbers to characterize the state of a quantum system, as many quantum numbers as there are degrees of freedom in that system, then we want to represent the wave function that describes a state of that quantum system, and the density that corresponds to that wave function. In the hydrogen atom, that is not straightforward, but at least imaginable, we have different solutions for the states of the hydrogen atom, and in the hydrogen atom, depending on

what you consider, you have 3 or 4 degrees of freedom, if we neglect spin, we have 3 degrees of freedom for my single electron, if we use the Born-Oppenheimer approximation, and that means that if you want to represent the value of the wave function, which is a complex number, you have to display two things, as a function of 3-dimensional space, so you would need two 4-dimensional pictures. That's not possible, so already there, for the very simplest system, you have to play some tricks to represent these wave functions, we call them the orbitals of the hydrogen atom, and people make various choices, isosurfaces, cuts through space, and that leads to pictures of the type you see here on this screen. Why do I show these hydrogen orbitals? Because often you will represent a quantum wave function, a many-particle wave function, as a sum of such one orbital states. So let me summarize this from the very beginning, in a systematic way. I already told that every configuration that a quantum system can take is labeled by a unique set of quantum numbers, there are as many quantum numbers as there are degrees of freedom in the system, and my example is the hydrogen atom, so with the Born-Oppenheimer approximation applied, the electron has three spatial degrees of freedom, one spin degree of freedom, you need four quantum numbers, and every unique choice of these four quantum numbers represents one state of the hydrogen atom, and if you now look at an atom with more than one electron, so all other atoms of the periodic table, then, it's much more difficult, you cannot easily draw anymore how these many-body states look like. It was already problematic for the hydrogen atom, it's almost undoable for these more complex atoms. And therefore, in order to have at least some way to visualize some aspects of that, it turns out you can use that many-body wave function onto one-particle solutions, and apparently in the many-body wave function for such a complex atom, you recognize a contribution that looks very much like the 1s orbital in a hydrogen atom, and a 2p orbital as in a hydrogen atom, and so on. So it's not telling everything, but a lot of information is present in these one-particle projections of the many-body wave function. We are so used to that in atomic physics that we even don't actively think anymore what these things mean, but it's good to realize this once again, to understand what happens then in solid-state physics in crystals. In solid-state physics 2 we will have four quantum numbers that define a one-particle orbital of a crystal lattice. And we will project the many-body wave function onto these one-particle solutions. We will come to that in a few slides. I first still look at the hydrogen atom, because you visited probably the Orbitron, where you had some visualizations of these hydrogen one-particle states, where every year there are people who have a hard time figuring out what exactly that means. So therefore let me run through this with a few extra explanations. You see a cut in a plane through the hydrogen atom, so this horizontal plane, and for every point in the plane, you put the value of the 2px wave function in a particular convention such that rather than a complex number you can plot one real number. And you see that for some parts of the plane and for other parts it's positive. The picture here is exactly the same, but rather than on a plane you have just one line through the hydrogen atom. So the nucleus of the hydrogen atom is here in the origin. These are wave functions. You can take the modulus squared and get densities out of that. And there you have three different representations. Again, in the same plane through the hydrogen nucleus you have now the density for every point in the plane and densities are always positive. If you take a line then it's this curve and now you take a particular value of the density so you take you slice this picture here and you say on the plane every point on that horizontal plane where my density reaches this particular value that one I will color. So if I would draw that plane here the points here that are colored are the points on the plane where that value is reached. In a line slice it would be these few values. You get an isosurface of all points in space you do this because this is a way how you can visualize a wave function in space. You take all points in space where the density reaches one particular value. And this gives an idea of the shape of the density that corresponds to that wave function. You see this is an entire struggle to get a visual representation of something that you cannot visualize because it lives in too many dimensions. But we do that for atoms we will also do that for crystals. So for crystals we need now quantum numbers just as we had our quantum numbers for the atoms. For the crystal that was the last video of the past week. And we do that by looking at our first Brion zone. Let's first count how many degrees of freedom do we

have in our real crystal with the Born-Oppenheimer approximation made so I only look at the electrons and the reasoning is summarized there in the text at the upper left. We have  $n$  unit cells in a macroscopic piece of crystalline material in every unit cell we have  $m$  electrons so there are  $m$  times  $n$  electrons in the entire crystal and every electron has 4 degrees of freedom 3 spatial 1 spin so that's 4 times  $n$  times  $m$  degrees of freedom and that will be a huge number of the order of magnitude of Avogadro's constant so how do we find that amount of quantum numbers how do we represent that amount of quantum numbers and I don't derive it I just give you the result of the procedure the result is you take the first Brion zone you take  $n$  points in the first Brion zone and remember what  $n$  was is the number of unit cells in the macroscopic piece of matter so order of magnitude  $10$  to the power  $23$  points which already means that these points are very very closely together this is almost the same as a continuous sampling of the first Brion zone so  $n$  points in the first Brion zone every point indicates a vector, a wave vector so 3 coordinates 3 components and every component represents 1 quantum number so we have 3 times  $n$  quantum numbers already and then we have per such vector a number of bands if you think in terms of the band structure which is a picture where you take 1  $k$  vector and then you go up to the energy axis and you reach several lines these are the bands there is a whole story about this this is folding of the more remote Brion zones back onto the first Brion zone because you can represent these quantum numbers in many different ways but the conventional picture of the most often used picture is concentrate on the first Brion zone and have a number of bands  $k$  vector in the first Brion zone so  $3n$  times  $m$  and there is also this spin degree of freedom that gives you 4 rather than 3 so indeed in this way we can find 4 times  $m$  times  $n$  quantum numbers always represented by a  $k$  vector in the first Brion zone a band index so which band for this is it? and a spin quantum number plus or minus up or down so this huge collection of vectors and band indexes and spin indices that is our set of our enormous set of quantum numbers for a crystal and now we have to make pictures out of that for an atom so how do we do that? we start from the unit cell of our direct crystal we transform that to reciprocal space to see the first Brion zone all our  $k$  vectors live in the first Brion zone so we take a path a linear path which is a concatenation of some line segments through the first Brion zone and for every  $k$  vector along the first Brion zone we give the energy of the band the energy of the wave function the one particle wave function that is represented by that set of quantum numbers so I go here in the picture for instance from gamma to  $x$ , that means in the first Brion zone I start at gamma there are a number of  $k$  vectors along this path an infinite number well in reality a finite number but so densely spaced that this is continuous so I take one of these numbers I calculate the eigen values the eigen energies for the one particle solutions with that  $k$  vector and I find several values namely the several bands that are possible for that quantum number so the band structure picture that you find is a way to characterize some aspects of the wave functions the one particle wave functions for the crystal a very limited aspect you will not see how the wave functions look like in space no, you just have their energies such as you would have the eigen values of an atom the energy values of an atom these atomic energy diagrams so you have that information an alternative way to do this is not to take such a path through the first Brion zone but to consider all points in the first Brion zone so the really almost infinite set of  $k$  points to calculate for all of them the energies the eigen values and to make a histogram of how many times do I meet that particular energy and that gives then rise to such pictures which is known as the density of states more precisely the density of energies of states and these two ways of representation are related in the band structure the energy axis is the vertical axis in the density of states the energy axis is the horizontal one but that means if we turn around the picture of the density of states such that the energy axis is vertical and we align the energy axis then we can see that the density of states will be zero and it starts to be non-zero from the place onwards where you have bands if there would be a gap somewhere in the band structure there will be no density of states in that position and in this way you are able now to use quantum espresso to draw your band structures any crystal you want and some years ago somebody was very excited about that and said yes now we can even make pictures that would not feel bad in a textbook and I found that a very interesting remark because indeed a few generations ago the people who were studying



solid state physics they knew band structures only from textbooks it was very expensive very cumbersome to create a band structure picture and you could not hope if you were studying anything else than one of the typical easy crystals you could not hope to find a band structure picture but now with these DFT codes that are around the world you can do it just as a reminder because even if you don't work routinely with band structure pictures as detailed as the ones you just saw here you may work with band structure pictures that are more cartoon like you distinguish only between regions where we do have bands energies and regions where there are none and I think this picture here was the silicon band structure so if you are in this region here where the silicon bands are occupied by electrons that is what you called the valence band the unoccupied region at the ground state at zero kelvin that is the conduction band and the band gap of silicon in between these two where there are no states at all so this is how you can see from a band structure whether you deal with a metal or an insulator silicon is an insulator a semiconductor but that is just an insulator with a small band gap and you have many of such cartoon pictures if you google for it the band structure the detailed band structure is the underlying physics where these cartoon pictures came from I finally asked you let's now do some computer experiments we take our we take a crystal here FCC aluminum a very simple metal the band structure the actual band structure is on the left hand side and now I make artificially my lattice parameter larger and you see that these bands become more and more flat so why is that why do they become more flat and why is the 3s band more rapidly flat than the 3p band oh this was the last year that I forgot to erase not relevant this year so here you see one of your answers let me read it with you as the lattice parameter increases the atomic orbitals on neighboring atoms overlap less in the limit where the lattice parameter approaches infinity the atoms are so far apart that they are isolated atoms there is no overlap anymore and you would need to find back the picture of a single free atom so all these k vectors that all have different eigenvalues that is because you have a crystal because these atoms interact with each other but if you have only three atoms identical aluminum atoms that do not feel each other anymore you should find only one answer the energies for a single aluminum atom and you can see if all these bands would be flat lines in the limit of infinite separation that is what you get regardless at which k vector you look you find the same energy values so that would be the energy spectrum for a free aluminum atom so the picture of quantum numbers for a crystal with interaction between the atoms and quantum numbers for a free atom where all identical free atoms have the same energies these two pictures they seamlessly evolve into one another these are not two different ways to look at the situation it is one way and by playing with the lattice parameter you can bring one picture into the other why is that 3s orbital more rapidly flat than the 3p one of you formulated it this way because the 3p orbitals they are more extended so you will need a lattice parameter to decouple these orbitals from each other they will overlap more easily with the neighboring atoms and you need a larger lattice parameter to make them not overlap anymore and this was an answer not from this year but from a previous year and I keep it because it tells me that if the lattice parameter increases the size of the unit cell at least in volume increases the number of atoms in the unit cell remains the same that means distances in direct space increase and in reciprocal space my first Brighouin zone will get smaller and smaller in the first Brighouin zone because remember you need as many k points as there are unit cells in my original crystal the same very large amount of k points in a unit cell in a Brighouin zone that is shrinking and shrinking means that in the end all k points in the limit all k points will fall on top of each other you will have only one k point only one k vector and therefore all the eigen energies will always be the same because whatever k point you take you effectively always take the same k point so you have a flat line if you plot always your energies as a function of the k point you chose so a different way of reasoning but very consistent very insightful that is it for the feedback on electronic structure so let us have a quick look at next week then we will go more in the direction of chemistry not solid state physics anymore but chemistry and we will look at chemical bonding from a DFT point of view good for this week now as usual please take some time to go to the form that you see here linked on the screen write your summary for this week and formulate an exam question so I will not let this play for 5 minutes just take note of the link and do

that so you can stop the video hereafter because I am done and as this is not live there is no opportunity for questions but once again if you have further questions about this topic put it in Zulip or put it in the question form and we can deal with it next week I am not sure about next week or event on my agenda but I am not sure is it Monday or Tuesday so it might be that also next week it will be pre-recorded I am sorry for that I hope it doesn't disturb you too much in any case in one way or another I will see you back here next week bye bye