Computational Materials Physics (2023-12-04)
Week 10 : supercells and surfaces, precision and accuracy

(automated transcription)

This is the feedback webinar on the last two remaining topics in this course, supercells and surfaces, and precision and accuracy. And this is once again a pre-recorded webinar, so I just looked at all of your tasks and well I will not be available on Monday afternoon and therefore I pre-record this webinar. Sorry for that. So what was the topic of this week? We looked at the concepts of supercells, that was the first part, and the confidence statement I can explain what a supercell is and why it is needed. And this gives me the opportunity to link this back to one of the topics we touched on in previous modules, the difference between primitive and conventional cells. Whenever you use CIFII cell in the default setup it will give you the primitive cell, which makes sense because you want to use this as input for a DFT calculation and therefore the smaller cell is, the fewer atoms there are, the faster the calculation goes. So CIFII cell will aim for primitive cells, but if you do not want to have the primitive cell, if you want to have a conventional cell for those lattices where there is a difference between both, then you can use in CIFII cell the option no-reduce. If you would apply this to a bulk BCC lattice, then it would give you the BCC cell, the cubic cell with two atoms. For the FCC cell, if you would apply it there, it would give you the cube with four atoms. You will need that no-reduce option a few times because when thinking about supercells, multiplying these cells in different dimensions, then it is far easier to think in terms of conventional cells than in terms of primitive cells. It's perfectly allowed to make supercells starting from primitive cells, if you know what you are doing. Good, there was quite a list of tasks to do with supercells and let's go through them one by one. The first one was to create a supercell for a single atom vacancy in ferrite. So first you had to get a CIF file for ferrite, which is alpha iron, BCC iron. Somebody noticed that the CIF file that was suggested was for delta iron, which is a high temperature phase of iron, but delta iron is also BCC. So the only goal here was to have a CIF file for a BCC iron phase, alpha or delta, that doesn't matter, the lattice parameter will be different, but for the concept of creating supercells, the value of that lattice parameter does not play a role. So with that WGET statement you get one of these CIF files, and then if you want to create this conventional cube, that's where you have to use the no-reduce option, I will switch to the pointer, then in the third step you can create a supercell, and here there is the statement to create a 2x2x2 supercell, so you start from that given CIF file, you give the no-reduce option, so you start from the conventional cell, and the supercell you make has this 2x2x2 size. We will come in a few slides to the exact meaning of these vectors here. We want to introduce a vacancy, so you have to delete one coordinate line to delete one atom, and the counter that counts how many atoms are in that file should then also be reduced by one. And if you have done that, then you have your supercell with a vacancy. If you want to do a DFT calculation with that, then you have to do the usual steps, go through FindSim to have the setting with the highest symmetry, but here for our visualization that does not matter. So here are a few specific examples, this is how it could look like with the deleted coordinates, if you get this particular message from X-CRIS, then if you want to visualize this, then this is because you did not reduce NOT by one. Another example, this was here an example with 8 atoms, so 8-1, 7 atoms, so that will have been a 2x2x1 supercell, this one here is a 2x2x2 with 16 atoms, and one deleted, so 15, this is an example where somebody just used the conventional BCC unit cell and deletes one atom, in principle that is a model for a vacancy as well, but if you repeat this in 3 dimensions, you will have just one half of the atoms of the original lattice, so you have deleted one half of the atoms, that is not the idea of an isolated vacancy. So for supercells that are meant to model point defects, like vacancies, your supercell needs to be reasonably large, and 2x2x2 is probably not large enough for realistic calculations, but your supercell needs to be sufficiently large in order to have the defects sufficiently far apart from each other. Here are some other examples where people used supercells, here 2x1x1 primitive supercells, where then an atom is deleted and you see what you get is not really an isolated

vacancy. This was another example, somebody used a 3x1x1 supercell, then deletes one atom and indeed you see the vacancy here, but if you expand this in 3 dimensions you will see that you have one entire layer of vacancies, so not at all isolated vacancies, an entire monolayer of vacancies, so not a good model for a vacancy in an infinite lattice. There were also people who were struggling with how to put a vacancy somewhere, I said delete a coordinate, and once you know that, that is obvious, but it is not so obvious if you have never seen this instruction, so some people put their atoms with special symbols like VA, or give the mass of the atom the value 0, which are indeed smart tricks to get a vacancy there, but this is not what Quantum Espresso will like as input. A vacancy is really a missing atom, so there should be nothing, no coordinate line, no chemical symbol, nothing. And I said for a true isolated vacancy you have to make your supercell larger, so this is an example of somebody who made a 3x3x3 supercell with a vacancy, or a 5x5x5, the vacancy is here at the corners of the unit cell, so this would be good input for more realistic calculations, but time consuming calculations. There was even, and I think this is something I kept from a previous year, somebody who suggested to do a manual construction of the unit cell, of the supercell, which is perfectly possible, but you have to type all these coordinates yourself, and that is not only a lot of work, but also something that easily can lead to typing errors, so not the recommended way. If you do not use CIF2CELL to create your supercells, then it is also possible in VESTA, so it is indicated here how you can get to this menu in VESTA, where you can also give these kind of supercell transformation matrices, which contain the same three vectors that you have in CIF2CELL in the command, but here arranged as a matrix. And somebody suggested to use ASE, which is another useful tool to do all kinds of manipulations with input files for DFT codes, including creation of supercells. I do not touch ASE in this course, because using ASE requires some familiarity with Python, which you do not necessarily have, but if you are comfortable with Python, then ASE definitely is a good tool that you can use in combination with a lot of DFT codes. A question that somebody once asked, and that is an insightful question, if you have to delete such a coordinate line in order to create a vacancy, does it matter which coordinate line you delete? In a BCC cell with 2x2x2 size, you have 16 atoms, does it matter which of these 16 I delete? And the answer here is no, for this specific case it does not matter, because there is only one Wyckoff site in BCC-IRNN, so every atom is equivalent to every other atom, so which one you choose as the vacancy, that does not matter. If you would have to introduce two vacancies in that cell, then it would matter, the first one still does not matter, but the second vacancy, do you take that close to the original vacancy in its first neighbor cell, or as far away as possible, so these are different possible choices. Good, so much about that first one, creating a vacancy in ferrite, then the next task was create an interstitial impurity in ferrite, put an interstitial carbon atom in ferrite at the octahedral site, and it was here indicated what the octahedral site means. Somebody said I do not delete now an element, I rather replace an iron atom by a carbon atom, that would be a substitutional impurity, which can, that is a situation that is often possible, but here we did not ask for a substitutional impurity, but for an interstitial impurity. So you cannot just replace an atom by another one, you have to introduce new coordinate lines. We will show what exactly, but first somebody who tried to do it in another way, so in Vesta, remove one of the atoms from the picture, well there are several problems with that in the first place, this is not a cell, this picture does not represent a cell with periodic boundary conditions, if you have deleted this carbon atom here. It is a correct interstitial carbon, but if you use this cell as your unit, then you need periodic boundary conditions, so you cannot just delete that atom here. So this would not lead to valid input for a DFT file, for a DFT code, so you have to leave that atom, if you take this as your unit, so this would indeed be a valid representation of an interstitial carbon, but in a very very very small supercell, just the conventional cell. So you need to add one coordinate line, you have to increase the number of atoms by one, and you have to increase the number of types of atoms, the number of elements also by one, because now you have iron and carbon, two elements, so that needs to be reflected there. I said this is a very small cell, you need more dilution, so you could do this in a 2 by 1 by 1 cell, that is already somewhat more diluted, or you can take a 2 by 2 by 2 cell, and there it starts to be more realistic. This is an illustration that if you use a 2 by 1 by 1 cell, and you look at this picture in three dimensions, so here there are a few more of these unit cells given, then you really see that you are creating layers of iron and carbon, so perhaps not the idea of an isolated interstitial impurity. And why did I put this

one? Here at the left you had a 2 by 1 by 1, this is a 3 by 1 by 1, so you separate the distance between the carbon atoms in the vertical direction, but they remain as close to each other in the horizontal direction as it was in this case, so if your goal is to make carbon atoms that are far away from each other, you have to take more cubic types of supercells. The next task was to create a supercell for surfaces, the 1 0 0 and the 1 1 0 surface of ferrite, and demonstrate that these are indeed two different surfaces. For the 1 0 0 surface I give here the full statement for CYF2Cell, and this was not for everybody obvious what this statement exactly means, so therefore let's walk through the meaning of these vectors and the vacuum. We start from a choice of axis, so the XYZ axis system in which we work is an axis system that is connected to the BCC cube, so let's say that this direction is my X direction, this is the Y direction, and perpendicular to the screen is the Z direction. Now I take a supercell that is in the X direction 5 times longer than the original cell, so if this is my original cell, as you see it here in blue, starting from the origin, 5 times that cell in the X direction, 5 times in the Y direction, 5 times in the Z direction out of the screen, so you have really a cube here, and now I introduce a vacuum in the third vector here, so perpendicular to this vector you introduce a vacuum slab that has a thickness of 1, 1 in terms of the length of this vector. So practically this means you intersect this picture in the horizontal direction and you squeeze 5 lattice parameters of a vacuum in that vertical direction. You will see that even better if we go to the 1, 1, 0 surface where I create this type of supercell, so we go 3 in the X direction, 3 in the Y direction, 0 in the Z direction, that's the end point for my first lattice vector, this one here, the other one, minus 3, 3, 0, minus 3 in the X direction, plus 3 in the Y direction, 0 in the Z direction, that's my second one, and the third one is perpendicular to this, comes out of the screen. And now I introduce my vacuum in the second vector, so this one is here the second vector, so perpendicular to the second vector I introduce a vacuum, it would be as if you would cut this crystal here and then take these two parts apart from each other such that you can introduce here a block of vacuum, a block of vacuum that has the thickness, the same thickness as the length of this vector. So that is the meaning of these three supercell vectors, and if you make a matrix out of that, that is the supercell transformation matrix that you can use in Vesta. And if you do that for the two types of surfaces then you see that indeed in that surface layer the atoms are arranged in different ways, so these are indeed two very different surfaces. And a few years ago this triggered this statement in one of the students of that year, a statement that I can relate to, indeed once you feel comfortable with generating all these kinds of supercells then you feel like you can create materials at wish. Here are other examples, a 1 0 0 surface and a 1 1 0 surface. Of course if you want to make realistic calculations, depending on what you want to do with these surfaces, if they are clean surfaces then you will make them as small as possible. So this is a 4 by 4, 1 0 0 surface, on the previous slide you had a 1 by 1, 1 0 0 surface, so if it is to model the clean surface then this one here is good enough, you do not have to do the more expensive calculation of this one. If you want to put an isolated impurity on the surface then of course you need the larger one. Here again you have the instructions for Vesta, but if you want to make surfaces in Vesta then you have to delete the atoms that are at the position of the vacuum manually. And this is how you could make the minimalistic supercell that can model the clean surface with as few atoms as possible. If you are searching to make a realistic model for a surface then you have to do some kind of convergence testing again, but now not convergence testing for mathematical parameters, no they are now for more physical parameters, like what is the thickness of the slab. You have to make your slab sufficiently thick such that one surface of the slab does not interact with the other surface of the slab. So keep adding layers until these two surfaces are decoupled. And similarly for the vacuum, the vacuum should also be sufficiently large to prevent that one surface interacts with the other one through the vacuum. So also these two properties have to be tested. Keep increasing them until results do not change anymore. Now on top of these surfaces we will add extra atoms. For instance replace one of the surface atoms by an impurity atom, a copper atom for instance. You have to find a coordinate line that is in the surface and replace that by another element. If you want to add that element on top of the layer, on top of the surface, then you cannot just replace something. Somebody here did the trick, well I keep an extra layer and then I delete everything except for the atom that I want to replace and that is a clever trick. But that only works if that extra atom will be at positions where that original atom was. And there is no need why that should be. On a surface you

have much more freedom. You can put the atom basically wherever you want. We will come to that in a few minutes. So here are two visual examples of an impurity atom that is inside the surface layer or one that is on top of the surface layer. Here are other examples. This is a supercell where something differently happens. This is a supercell where something differently happens. So if you would extend this in all dimensions what would you see? A model for a surface but that surface is covered by a model layer of another element. And that can be something you want but if your goal is to have an isolated impurity of that other element of course this is not good. But a perfect model for a real monolayer not for an isolated surface impurity. And if you have visualisation problems in X-CRIS-DEN then just check whether you did the right thing with the NOT and the NTIP keywords. If you did not increase or decrease them as it should then X-CRIS-DEN may refuse to visualise. Here it is summarised. If you have an impurity atom at a position where there was already an original atom then NTIP has to be increased and you change the element symbol. If you put the extra atom on top of the surface then not only NTIP has to be increased but also NOT has to be increased and you have to add a new position line. At this point you may wonder I put an extra atom on the surface but where should I put it? And that where that can be in the horizontal direction or in the vertical direction. So if I look on top of the surface I could put my impurity atom at that yellow position such that it falls into the square by these four surface atoms that is called the hollow side or you could put it on the bridge side where it is on the shortest distance between two surface atoms or even on the top side where it is directly on top of a surface atom. And everything else in between in principle any position in two dimensions is possible. So yes you will have to make a choice there and if you don't have any extra information it means you have to do all of these possibilities and see which one gives you the lowest energy. That is for the horizontal direction but also in the vertical direction you have to determine where you put your atom. You can put it high above the surface or very close to the surface and everything in between and there too you will have to do an energy versus height optimization or bring the forces to zero that is equivalent. The minimum in the energy curve or the position with zero forces you have to calculate this yourself, you cannot know this in advance. And the last task in this series was to create a 001 surface for a rock salt crystal with some specifications, seven layers in the slab, some vacuum, it is not specified which one and there is a silicon atom on top of that surface at a position where there was a sodium or chlorine atom before. And the periodic copies of that silicon atom they should be four lattice parameters away from each other. Good, in order to see how to count let's first look at the rock salt unit cell. You have here the rock salt unit cell and I wonder how many layers do I have in this cell? How many layers does this cell represent? If you look at the picture you would spontaneously perhaps say three but that is not fully correct because the periodic boundary conditions play a role. Every atom in this bottom layer is only for one half inside that cell and the same for the top layer. So these two layers count for one half and the central layer is completely inside the cell. So this represents two layers and that means if we want to have seven layers then we need at least four of these conventional cells. Four times two layers that would be eight layers and then we can delete one of them but with less than four stacked unit cells it will not succeed. Here is an example of a solution. So you take four times that unit cell. Here it is a two by two by four unit cell. You introduce a vacuum in that C direction. You remove all atoms from layer number eight except for one that will then become the position of the silicon atom. Here you see the silicon atom and the only thing that is not right in this solution that is that now I asked the silicon atoms to be four lattice parameters away from each other but this here is the original rock salt unit cell. So you see that this cell here has only two lattice parameters as an edge length. So that is not correct. You should have rather something like this. This is a cell where we have four lattice parameters in the horizontal direction and my red silicon impurities are now four lattice parameters away from each other. Here is another example with the comment that can create the correct cell for you where then we have to delete in layer number eight all atoms except for one and that remaining atom you turn into silicon. And then it looks like this. In the visualization of such a cell with X-chrysden somebody noticed well my picture does not look nice because the silicon atom in X-chrysden has the same color as either the sodium or the chlorine atom. There is a solution to that. If you go in X-chrysden to the menu modify atomic color then you can select all the elements and you have an RGB color bar here where you can give an arbitrary color to

every different element. And here too there were people who add the silicon not as an isolated impurity as it was meant but as a monolayer. So again that can sometimes be what you want. I just add this here as an extra warning. Check before you set up the cell do I need to model a monolayer or an isolated surface impurity. And this is an example where somebody said well I put my silicon atom exactly in the middle on the top layer such that there are four lattice parameters apart horizontally. That is correct but you are not restricted to putting it in the middle. You can equally well put your silicon atom exactly in the middle and you can equally well put your silicon atom here at the very corners and there will still be four lattice parameters away from each other. Actually for every position you take in the horizontal plane there will be four lattice parameters away from each other, the periodic copies. So there horizontal position does not matter too much. Well does not matter at all. That was quite lengthy about working with supercells. Now we will do calculations with supercells to get properties out of this. And somebody complained in one of the forums well it was again calculating total energies. Yes that is very often what you do with the functional theory. Many properties can be obtained from calculating total energies. So that is something we do a lot. And what we calculate here, surface energies and work functions were the two targets. First the surface energies. You have to take a BCC001 surface for vanadium. I gave you a very small supercell for this, just with three layers. And the goal was to calculate the forces on the surface layer. And this is what you get in this axis system here. It is important to see where the z-axis is pointing. This is the z-direction and the origin is here. So positive z-direction is upwards. That means that the central layer, the one with the atom at 1.5, 1.5, 1.5, 1.5 in the z-direction. That central atom is here. Then you have one at 000.6 so we have to move in the positive z-direction. This is this atom and the third coordinate is this atom. The forces on these atoms, they are brought in the output in the same sequence. So that second atom in my list, this atom here, has a positive force. So the force vector is pointing in this direction. While this atom has a negative force, the force vector is pointing in this direction. And so if you know that the forces are pointing up and down, then the question is how will the atoms move and here the answer is they move towards the vacuum. Which somebody says is a bit counterintuitive. Not everybody agrees because somebody else says the atoms are moving towards the vacuum and this is what I intuitively expect. Well, what could you intuitively expect? What is the correct physical intuition? It's a situation that is analogous to surface tension. At the surface, the atoms that are at the surface in a liquid, they feel the attractive forces by the other atoms or molecules under them, but not by the ones above them because you have vacuum there or air. So therefore there will be an extra force downwards. The surface will tend to contract. That is the surface tension. And this vanadium layer, these two vanadium surfaces, they were behaving in exactly the opposite way. The atoms move towards the center. Why is that? Well, purely because that supercell here is so artificially small. If you would take seven layers in this lab, then no doubt the top layers would come down towards the center. And that is indeed what somebody noticed and this could be due to the simplicity of the model that we used. Somebody wondered why do we use such a small layer. I thought that this is not at all realistic since we have no bulk material in here. We have just one surface that is interacting with the other surface via this very thin intermediate section. So this is not a good representation of a true surface. The reason is, somebody complains that this calculation takes quite a while. If you would have taken a realistic model, the calculation would take even longer. You were asked to determine the surface energy for this surface with and without optimizing the positions. The actual question was without optimizing to save time. But there were people who did the optimization as well. This is the expression for the surface energy that we have to use. One half, because in a slab you have two surfaces and you calculate the energy from the slab and you subtract the same amount of atoms as there are in the slab but now with the energy they have in the bulk. And this is how somebody... slab minus some energy in the bulk and that gives a value of hundreds of Riemberg which is totally unrealistic. Surface energies are much smaller than that, smaller than one Riemberg, smaller than the order of magnitude of a few eV at most. Something went wrong here and the thing that went wrong is the counting. If this is the energy of a conventional cell, so with two atoms, you need to subtract the same amount of atoms as there were in the slab and in the slab we had three. So, rather than one we need 1.5 here, 1.5 times the energy for two atoms, that's three. This is how a correct calculation

would look like. If you look at all the numbers it gives you 12 mR per square angstrom as surface energy, 2.7 J per square meter. These are typical values for surface energies. And here you have the results in many different units, so hopefully you find the unit there that you used in your calculation. What would then happen with the surface energy if you optimise the positions? Would the surface energy increase or decrease? I find answers in both directions. Some say it will increase, others say it will decrease. You can reason about this in a mathematical or in a conceptual way. So here is the mathematical way summarised. You have the energy of a slab not optimised minus the bulk gives you the surface energy. And surface energy is a positive number because it costs you energy to create the surface. And this is then the optimised slab minus the bulk energy gives you the surface energy for the optimised surface. Because the energy for the slab and the energy for the bulk are negative numbers and because the E' the optimised energy is smaller than the non-optimised energy of course, because these relations are fulfilled, the surface energy with optimisation will be smaller than the one without optimisation. So it is the decrease that is correct. And that follows spontaneously from these numbers but you can also look at it conceptually. Introducing a surface costs energy. If you then optimise the positions of the atoms that lowers the energy again. So the energy cost, the final energy cost of creating the surface will have been diminished a bit. So smaller surface energy if you optimise the positions. And if you would want to do the actual calculation for this optimised positions, how would you do that? That was the next question. And now somebody suggests optimisation. Let's do a VC-RELAX and we're done. Yeah, but for surface cells, so slabs with vacuum, this will not work. Because even if the VC-RELAX algorithm would be very universal and if you would apply this to a slab, what will it do? It costs energy to create a slab. So the lower energy situation is the one where there is no slab at all, where the vacuum has been removed to become zero. So with a VC-RELAX with a variable cell where you can adjust the shape and the size of the unit cell, you can adjust it in such a way that you get rid of vacuum and then your crystal is optimised, but you have no surface anymore. So VC-RELAX is not the good option here. Someone else says, well I don't know how to do it, but maybe there are ways to optimise just the X and Y parameters, so the A and B lattice parameters and not the C lattice parameter, because that is the one you need to keep for the vacuum. That will not work either, because in a realistic slab, the slab is sufficiently thick such that the centre of the slab can be the bulk material with the bulk lattice constants. And that was cubic here, so you don't want to play with this A and B direction, because otherwise you would give a different lattice parameter and even a different qualitative geometry to the material in the bulk in the centre of the layer. So the message is, if you do optimisations for a slab supercell, don't touch the slab size and shape. The only thing you are allowed to fix is the positions of the atoms. And even there, it can be that you want to keep some atoms at fixed positions, for instance if you want to force that the centre of the slab is as bulk-like as possible, even if the atoms close to that centre would want to relax a bit, because the surface layers have relaxed. So how do you do that? Fixing positions, that is quite straightforward. If you look in the keyword file for Quantum Espresso, you can add extra numbers at the right-hand side of the coordinates, and if these numbers are 0, it means that component of the coordinate will not be changed, it will not move. Only if there is a 1, it is allowed to move. Now in this specific case, moving the atoms in the horizontal directions is just not allowed by symmetry, so we could even explicitly put a 0 there, or not put a 0 there, it will not matter, but just as an illustration what you should do if you want to keep atoms at fixed positions. Then the other property was work functions. Work functions are not too familiar for all of you, therefore I want to just remind you to the photoelectric effect, a very famous effect in the history of quantum physics, and that is one where the work function matters, because what does the photoelectric effect tell you? It tells you that if you have incoming light with a wavelength that is too short, that incoming light will not be able to kick out an electron from the crystal. It is only when you are above some threshold energy that electrons are ejected, and that the energy that they get gradually becomes more and more. This discrete step, that was a surprise in early quantum mechanics. We now know this is the energy that is needed to get from a valence band to the conduction band. Now that energy, that is also called the work function, and it was this one that you were suggested to calculate if you want to invest time in it, because it is less easy for the work function, but some of you tried, and this is a picture of the average potential, the red line, in the slab.

So here in this oscillating part you have three layers in the slab, and it is the value here, as far away from the slab as possible, that gives you the work function. Someone else has put it in words here, and you find a work function of about 3.8 eV, which is reasonably close to the experimental 4.3, especially given the fact that we use a very, very small supercell here. So much for the first part, supercells and surfaces. Then precision and accuracy, where the opinions are a bit split. It is a lot of work, and you had this long video there, and with supercells we can do more spectacular things. So you are not a fan, or not all of you are a fan. Okay, I can only observe that, still it is a useful topic. Confidence statements where accuracy and precision, do you know what these two concepts mean, and do you understand the difference? Seems to go quite well. I asked you to have a look at a database of so-called delta values, which are differences between DFT codes that do calculations for the same crystal, in a specific kind of test, that was called this delta value. The only reason for this exercise was to bring you to the page with that information, and to bring you in touch with that. I should add here, and especially this year, that the page that you visited was based on our first publication on this topic. Now just one month ago we have a new publication in Nature Reviews Physics, where we extend this concept of these 71 elemental crystals with a delta criterion. It has been increased to 960 crystals, which covers all the elements, and every element in 10 different environments. So that makes this a dataset that is ideally suited to test the precision of pseudo-potentials. So you can do this calculation with a non-electron code, and the same calculations with a plane wave code with a pseudo-potential, and see whether or not they exactly agree. And if they do not agree sufficiently well, you may try to improve your pseudo-potential. And if that then successfully works, then you have a plane wave code that is just better, that reproduces all the electron results more faithfully. Moreover, in that work we also presented other quality measures rather than this delta criterion. There is now a quantity called epsilon that has a few properties that are just nicer. So if you are interested in this topic, then you can go to this paper, and it is linked to a website where you have the database of all the 960 crystals with all the different codes, and you can interactively play with that one as well. Second question was, well, this testing the precision. You have done this already, and obviously almost everybody found this. That was what happened during the convergence tests. Convergence tests are actually precision tests. You crank up your numerical settings until the values will not change anymore, until you have reached the ultimate precision. That does not guarantee that you will get close to experimental values, because that is accuracy, and it is not because you have great numerical precision that you should find results that are close to experiment. That depends on your own underlying theory. In the first place on your exchange correlation functional. So you can be as precise as you want, but that does not help you about accuracy. Then there was the friend who can do calculations with a fast computer. Is that better, is that more accurate than you can do it? Can this friend be closer to experiment than you can do it? And you agree that this is not the case. The result of that friend will be there faster, but the value of the result should be the same as the one you can generate on a slow computer. However, fast computers are not useless, and there were some good thoughts about this by one student of the previous year, so I keep that description here. If you have a fast computer, then it is easier to try out different things. You can try different exchange correlation functionals for instance, and see whether there is one that would describe for your particular problem the physics better. If that would be a very slow calculation, then you will be less tempted to do so. Fast computers have also advantages. And then the last question here was, go back to the litharge crystal, the lead oxide that you studied a few weeks ago, and do this error bar calculation or error bar estimate that was described in the papers. And here I have the result by one of you. You find a residual error of a final conclusion 22.0 ± 1.1, whereas the experimental value is 21.0. So this is within the error bar, but only just within. So this is a rather large deviation. And somebody acknowledges this. It is indeed quite bad, this agreement. Well, it is still just acceptable, but it is of the larger kind. And this person added, I have no idea why that litharge crystal would be special, such that you have such bad agreements. The answer to that is in a paper that I quote here, where it is explained that in the litharge crystal you have these layers of lead oxide, and within every layer you have strong covalent bonds, but the layers are bonded to other layers via Van der Waals interactions. And these are the ones that are not well described by our current exchange correlation functionals. So that is where DFT goes wrong. Especially the C lattice

parameter will be not described well. And we have touched that already in the general video about precision and accuracy, because the elements here at the right hand side, where there was not so good agreement in lattice parameters for instance, these were the ones that were bonded by dispersion forces. And that is just not what DFT is made for. These were the points that were in these correlation plots that were clearly deviated. There were a few people who wondered how can we get these zero point corrections. Well, often you can just neglect that, because for the error bar it will be such a small extra contribution that it is negligible. But if you do not want to neglect it, the way how we take it into account is, I will go to this paper here, it is an open access paper, and you will find these classical estimates for zero point corrections. So this is the expression for the zero point correction to a cohesive energy, and it depends on the Debye temperature, which itself depends on properties that we can calculate for the static crystal. So this is just for the cohesive energy, but in that paper you find zero point estimate formula, also for the volume for instance, or for the bulk modulus. You can find, if you wonder how do I determine these zero point corrections, you find approximate equations in that paper. Good, that has brought us to the end of this feedback webinar. Let's have a quick look on next week, because next week no new physics will be touched anymore. For the people who do not do the project, the work stops here. The people who do the project, they need one final sprint, or one final intense week, because next weekend by Sunday morning the project video and the paper is expected. On Monday I will give a webinar with a first discussion about the different results you obtained, and then the peer feedback process will start, you will receive forms for that, and you have then one week time to do the peer feedback. Because this is the last feedback webinar about scientific content, let me just repeat that those of you who are doing an exam, and who want to prepare for that and will probably have questions while studying, so how can you put these questions? The usual ways, you use the I have a question button, or you use the ZULU forum. If you want to have answer on this rather quickly, then it never harms to send a duplicate of the question by email, then you are sure that I have seen it and I can answer before the exam. And if there are questions there that are particularly relevant of general use, then I will add them to the frequently asked questions, which you find here and which are in general also a good study test. If you are somebody who does not do the project and who is a volunteering student, then here the course ends for you, and for these people I would encourage to fill out the feedback form. This is only meant for students who are not in Flanders or Belgium, because the ones from Flanders they will get different feedback forms at later stages. So please only this for the volunteering students. And the last link I show you is the one as usual, to suggest an exam question and to write down your few lines summary about the past week. As this is pre-recorded I will not wait here for five minutes, I just flash this and please fill this out. And with this this last content wise webinar can end. Bye bye.