webinar 5 – geometry optimization (part 2)

automated transcription

so this is the feedback webinar on the second part of geometry optimization and let us first start with some administrative and other information about the Bilbao crystallographic server and I have put on the Zulip thread about this temporary link where you can get access to the server again so this is a backup version that is not publicly shared but to which we got access for this course while the people in Spain are working to get the regular server back up again it's more than just hacking it appears to be a ransomware attack so they are in quite some trouble there it seems but thanks to that temporary link we can do whatever we need to do for this course not everything in the temporary version is set to be working but the basic functionality and certainly the things we need is there I have seen in your reports that several people pasted these green blocks with crystallographic information so which contains everything that this week was otherwise available at the Bilbao server and I wonder from where these came so if somebody who used this information can share the link with me then I will put that as an alternative link in the course site so just in case anything happens again in the future with the Bilbao server that could then be used in the future and be an alternative provided it is in publicly accessible site of course there were a few questions about running big cases and certainly related to the projects and well in case you missed it I point to what was explained in the webinar last week and which is also available on a Zulip channel in how you can enable parallel calculation and then we will see how to do that later in the course on your laptop so this will definitely be a help for big cases also something we will elaborate upon only in the coming week but that can already be useful that is how you can adapt your k-mesh how you can transfer this from small cases to larger cases if you have done a convergence test and you conclude that for the small crystal on which you did the convergence test you had and you need a 10 by 10 by 10 mesh well that mesh is fully equivalent to a 10 by 10 by 5 mesh for a similar crystal that is twice as large in the z-direction so if you double a crystal in one direction or a similar crystal that has more or less the same positions for the same elements if that one is twice as large in the z-direction then you need half as many k-points so if you would keep the 10 by 10 by 10 mesh for that bigger crystal it would take you more computation time but for exactly the same precision so therefore you can reduce that k-mesh and your calculation will be faster especially if you would have for instance a two by two by two increase of crystal that would be a 5 by 5 by 5 mesh so ten times smaller 2 to the power of three times smaller than the original mesh and therefore a calculation that is 10 times faster so if that applies to you then you can use that trick and if you have issues with disk space i recommend to look in the keyword directory of quantum espresso to the disk io and wfc dir keywords you have some options there to reduce the the size and number of files that are written during the calculation without affecting the results but with some drawbacks that you may need more ram memory and that you may not be able to restart that calculation afterwards so once it is done you have the output and you cannot continue from that point anymore but it will save disk space so if that should be an issue you can try to play with these i also saw a note that somebody wrote in the report that due to the feedback in the previous webinar this person discovered that there were many mistakes in that report and he or she had to redo everything and succeeded to get the correct output now but therefore there was not so much time for thinking deeply about the tasks of this week well this was apparently written down as an apology but I would take it as an example of the good spirit if you if the feedback helps you to improve well that's the best I can hope for so nevermind you have learned something that's very good and proceeds as as your schedule and time allows you to do so absolutely no bad feelings that there is then one week where you could where you could think less deeply good with this we can go to the scientific parts and the comments that I could read they fall in two categories there are people who are very enthusiastic who feel the power of this new knowledge who see how many new possibilities this opens but there are also people who say yeah you have to wait for a long time before these calculations are finished and preparing all these input files that can be tedious and yes I agree with the latter and but be sure that part of what we did in the past week is something you do only once and for a long time and that's what I would like to hear from you. regular calculations you will you will use templates or you will not do all these optimizations manually but it's good to have gone through the process once in detail to have a better feeling of what is going on this was the menu we were working our way through we had last week the initial steps volume optimization of our iron aluminium crystal cell shape optimization and in the past week you continued first piece of backgrounds of forces and then position optimization and finally that leads to face diagrams. on average most people seem to have succeeded to make all these exercises in this confidence diagram is towards the right hand side and well we'll go through this step by step first this background on forces in classical physics and quantum physics and we discussed here as a quick summary what is the major similarity and major difference between forces in classical and quantum physics the major similarity is that forces emerge as a negative derivative of total energy here in the Hamiltonian formulation where the Hamiltonian gives you the total energy in classical physics a force is some negative first derivative of a Hamiltonian translated to quantum physics if you know the potential energy of a force and you know the potential energy of a force and you know the energy surface or the Born-Oppenheimer surface which is the collection of all points in the phase space that have that give you for every point the total energy well if you know that surface in a high-dimensional space and you take these derivatives then you have the forces and the simplest example is the diatomic molecule depending on the distance between the two nuclei you have some total energy that is the red line in this curve so in this case the potential energy surface is just a line and if you take the negative derivative so the value of the slope of the tangent that gives you the force if you are here in this area of the curve the slope is positive but due to that minus sign the force will be negative so the force will be pointing opposite to this horizontal axis so if the separation is like this to the right hand side of the minimum then the nuclei will feel a force towards each other if you are in this area everything is the other way around and the nuclei will feel a force again towards each other but now in the other direction sorry not towards each other away from each other yes so exactly this same concept generalizes to a molecule or a crystal with as many atoms as you need just the dimensions of the space in which you draw this surface will now become much higher what is the major difference between the two? between forces in the classical and the quantum case that is how that derivative is calculated in the quantum case you need to take the derivative of a matrix element for the total energy operator which can be very complicated but which is thanks to the hellman feynman theorem not so complicated after all because these two outer terms here that are the complicated parts they cancel each other with this background of forces we started to do position optimizations of the atoms and these position optimization exercises these went quite well for most of you so most of you could do it being either completely sure or not so sure about the results but there were few people for which there were major difficulties and let's look at these results so first we have our orthorhombic iron aluminum cell space group 59 pmmn use that space group information to find which components of the internal position coordinates are not fixed in the quantum case by symmetry. So this was something where you had to use the Bilbao server, but most of you found a workaround for this. This would have been the table that you would have seen at the Bilbao server, and if we look at the positions of iron and aluminum, iron in the input file has this three quarters, three quarters, and then some number, and if we look here in the list, three quarters, three quarters, and then some unspecified number, that's indeed an iron position, and the other one, one quarter, one quarter, and the opposite of z, or in other words, the complement of z, that is the same, these positions for iron indeed correspond to Wyckoff's side, 2a. And yeah, the for aluminum, it's Wyckoff's side, 2b, with one quarter, three quarters, and some other value of z that is unspecified. If you look higher in the list, there are other sides that either have no degrees of freedom, or that have many degrees of freedom, all for the same space group 59. Okay, so we expect that we will see forces, in the z component for both the iron and the aluminum atom, and the question was to calculate these, and to inspect whether the size and the sign of these forces are in agreement with what we saw in this Wyckoff table. And here you see some results, so let's look at these one by one, we have this iron position, three quarters, three quarters, minus z, so that's this position, and this has a force, zero, zero, and then a negative value. So the force vector lies along the z-axis, and points downwards. For the other iron position, again, the force vector lies along the z-axis, and points upwards. And for the aluminum atom, this first one points downwards, and the other one points upwards. And in both cases, the upwards and downwards forces are the opposites of each other. That means, this last aluminum atom, that will have a coordinate, this coordinate of 0.5, 0.5, 0.8. Well, the force points upwards, so that coordinate should increase in value. Whereas for the first position, here the force is negative, so this coordinate will decrease in value. So, will that happen? Let's allow the relaxation process, the positions optimize, and we have the final coordinates, and in the last position, we have the final coordinates, and in the last position, we have the final coordinates. indeed that first position has decreased in value, the z-component of the position is smaller than it initially was, and this last one here for aluminum has increased. So the forces behave as we expect. Not for everybody though, there was a report here where there was a comment that somebody makes the opposite conclusion, and correctly states that this is against intuition, but if I look at the numbers, well, everything here is as I have shown on the previous slides. So these calculations were correct, it's probably only the interpretation that is wrong. So you see here an initial position of 0.916. An initial force of 0.916. A force that is negative, and a resulting position that is smaller than 0.916. So everything is correct, but the conclusion that the atoms do not move in the right way, that conclusion was not right. At this point, people often wonder, why do the forces obey these symmetry rules? And why is that even so in a code like QuantumEspresso, where there is no explicit symmetry information given? So you have typically P1 symmetry in a QuantumEspresso input file, and still the forces obey these symmetry operations. The reason is that for most positions in the crystal, if you would inspect the total energy, if an atom moves in the right way, then the forces would not move in the right way. If an atom moves slightly away from that specific position, in most cases, you will have such a parabola-like curve. So the position is really an equilibrium position, and there will be no tendency to break that symmetry, to go to a lower symmetry situation. 0.916. It is not excluded, however, that this happens, that you have some kind of spontaneous symmetry breaking. And if that happens, well, that will be in situations where the energy landscape looks like this. So you are, at this Wyckoff side, at a high symmetry side, there is as such no tendency to break the symmetry, at least not when, as long as you stay exactly at that position. 0.916. But if you move a little bit away, you fall to another minimum, where you do have this parabola-like shape. So if that is the underlying situation, then symmetry can be broken. So this does happen, this is possible, but the large majority of cases behaves like this. 0.916. A mistake that is sometimes made. 0.916. That, especially in this example, for iron and aluminum, with two Wyckoff sides where you have the z-coordinate that is unspecified, the value of this z-coordinate really is unique for every Wyckoff side. So don't make the mistake that you take the same z-value for both Wyckoff sides. There is absolutely no need to do so. Every Wyckoff side has its own freedom, independent of the other ones. 0.916. I also want to give a bit more hints on how to read the output, because you sometimes see coordinates in the output in fractional values, and sometimes in these units of a-lat. And how does that all connect together? 0.916. Well. It is very difficult once you have seen it. You have first of all the value of a-lat, that was specified here, and that is also specified in your input file. So everything will be given in units of this size. Then you go to the a-lattice vector, which in this case here is a unit vector. 0.916. The value. 0.916. The value of a-lattice vector is each of these components multiplied by the units, and then calculate the length as usual, so then you will have the absolute length of that lattice vector. 0.916. And the atom positions, they are given in this part of the output file, in a-lat units with respect to this lattice vector. It is indeed this position in a-lat units divided by this length of the lattice vector in the same unit, and if you would do that, if you would always express this with respect to the length of the lattice vector, then you would have positions in fractional coordinates, so from 0.2.1. 0.917. 0.916. 0.920. 0.90.. 0.90. 0.902. to the a lattice vector you can do the same for the b components with respect to the b lattice vector and their things so you can make this exercise and make the division you will see that that here your values will turn into either one quarter or three quarters and similarly for the C position where you will then find these two Z values okay so what are the final positions of the atoms after the relaxation we looked already at the final result but how far are these away from the initial positions and how much did the energy change you can inspect this if you look at how through the different SCF of through the different relaxations of the atoms you can find the Z values of the atoms after the relaxation we looked already at the final result but how far are these away steps how the forces evolved so you start at some nonzero value and you evolve to something that is basically zero and simultaneously the C coordinates or the Z coordinates of here the iron atom evolves from the initial value to this final value and nothing happens with the X and Y coordinates so this Z coordinate changes from this initial value to this final value so a fractional difference of 0.0142 and because this has to be measured in units of a lat times the C lattice vector this turns out to be 0.063 angstrom so a small but not negligible change of position of a few tens a few hundreds of an angstrom similarly for the energy the energy drops from five four three seven seven to five four nine nine so about seven milli Rydberg's in a unit cell with four atoms what does the value of a force mean when is a force large and when is a force small you have your forces in the output in Rydberg per atomic unit and if you have a force less than one milli Rydberg per atomic unit so two zeros and a one then it's basically zero if it is more than 10 milli Rydberg per atomic unit then this is a large force and typically a position optimization will give you a reduction of forces that are 0.0 something towards forces that are smaller than one milli Rydberg per atom per atomic units. If we inspect the volume changes in one of the reports there was a strange statement that the unit cell was initially 328 cubic Bohr or 48.7 cubic angstrom which is correct but that then upon energy minimization position optimization this would reduce to values that are almost 10 times smaller so very drastic change in volume and this is definitely not the case so I suspect that here something has gone wrong in translating the output lattice vectors to volumes because in another answer there you find a correct answer that there is a volume change of about 1.15 cubic Bohr so the final volume is about 330 and something so that is the correct value so a change of less than 1% in volume what is also useful for assessing in advance the complexity of your calculation that is to count how much energy you have in volume and how much energy you have in volume how many degrees of freedom there are and in this aluminum example we had two internal degrees of freedom we had these two Z values for the two Wyckoff sides and everything else was fixed by symmetry but on top of that for the the shape and size of the unit cell we have this orthorhombic box with an a B and C lattice parameter that are all independent from each other there are no symmetry relations between them so these are three other degrees of freedom so in total the aluminum the iron aluminum cell has 3 plus 2 has 5 degrees of freedom and knowing this so we have a system with 5 degrees of freedom how can you know mentally picture the optimization process it is like having five particles that can each move in one degree of freedom in some harmonic well that have friction and you shake the system you let the atoms the particles move and due to the friction they gradually slow down until they are at their energy minimum so the optimization process does nothing more than realizing that quantum that classical image in the quantum situation of a three-dimensional unit cell I have a look at the chat no questions there so far okay so this was position optimization not changing anything else not changing the volume not changing the shape of the unit cell if we go to what we called the full optimization procedure then volume and shape are changed and this you can imagine as optimization in a generalized potential energy surface where not only the nuclei move but there is also there are also degrees of freedom for the cell lattice vectors in order to to do that process efficiently that is only possible in DFT codes that have a stress tensor implemented which is something that is not in every DFT code easy it depends on the basis side the basis set that is being used the plane wave basis set of quantum espresso there it is easy to write down the stress tensor formalism and therefore we have a stress tensor in quantum espresso so you can do that automatic full optimization of all degrees of freedom at once that can be a long calculation but the advantage is it's fully automatic so you started you can forget about it and you can come back once the result is there just be careful to limitations so this is not something magical that will give you always the best optimization the lowest energy configuration of a crystal independent of your input no it will converge your crystal to the lowest energy configuration that is nearby your starting input think about our iron luminaire example we have we have in the end fully optimized it but we found another crystal the cesium chloride crystal structure that has a much larger a much lower energy so that cesium chloride structure is better than our optimized iron aluminum with the orthorhombic cell but that automatic procedure did not find it why because you start from the orthorhombic cell so it will find the best orthorhombic cell so the best solution that is nearby your starting point the cesium chloride solution was much farther away in phase space and is therefore not found by the automatic procedure so the automatic procedure fills in the details of the initial guess you have provided it with and this is an illustration of how the automatic procedure looks like in the output if you do the normal position optimization then you will still have a crystal with a stress tensor and if the size and the shape of the unit cell is optimized then you will have a stress tensor that is basically zero this is often yeah quite some information all these different minimization and optimization procedures and therefore let me summarize this part in an operational way so what do you have to fill out in the input files in order to get a particular result and well for the first two steps for the first two steps you have to fill out the input files in order to get a particular volume optimization and the cell shape there we only used total energy so that means you have a calculation of the type scf in your input file nothing changes to any geometrical value not to the unit cell size and shape and not to the atomic positions so and you only get a static total energy back that's enough for these first two steps if you want to optimize the atomic positions then you need not an scf calculation but a relax calculation so you need a different keyword in your input file and you need to add an ions block where the type of position optimization algorithm is specified the positions will be optimized but the volume and the shape of the unit cell will not be touched if you do the full optimization then you have to move to the VC relax type of calculation you still need the name of the algorithm that optimizes the atomic positions but you will also need to specify the name of the algorithm that optimizes the cell volume and the cell shape and you will need to give a target pressure well I think the default value is zero so if you don't specify a target pressure it will go to zero pressure as the target the equilibrium situation but if you want to find the best possible configuration for that crystal at a pressure of 1,000 kilobars and then you will need a different number so three different types of calculations SCF relax and VC relax always with an additional set of keywords in the input file that are needed and if you apply that full optimization then you will bring a crystal with these lattice parameters and these positions to a crystal with slightly different lattice parameters and slightly different positions. And if you look at these numbers, you might feel these are only small changes. Is it really worth the effort of going through that optimization procedure? And the answer is of course yes, otherwise we wouldn't spend time to do this for several reasons. One reason is that if you are after a really precise value of the bulk modulus, then you always need to do that procedure. Because the bulk modulus was found as the curvature near-equilibrium of the energy versus volume대burbe and here it was implicitly underneath that you always had the energy of the best possible crystal for that value of the volume. Which is, if you have a cubic crystal, there is no doubt, but in our orthorhombic crystal, imagine I have an initial configuration, an initial energy, I change the volume by just scaling the crystal size up or down, I track the energy as a function of volume, you will get that red curve. Wherever you are on that red curve, the b over a, the c over a ratios, they will be the same as in your initial structure. The atomic positions will also be the same as in your initial structure, they just scale together with the unit cell. So this is not the best possible crystal at any volume. If you fix a particular volume and you now optimize the crystal at that volume, you would get always a lower energy. And if you would do that for every volume, you would get for instance the blue curve. And that blue curve will have a bulk modulus that is a bit smaller, the curvature here is smaller. So in order to have accurate values of the bulk modulus, you need to go to this full optimization procedure. In the let's play section, there was an example of this for silicon dioxide. So here you have in two different colors, I think blue is the one without optimization and red the one with optimization. And you see that the red curve is slightly under the blue curve here. That's one argument. Why do we need this optimization procedure? Another argument is in the phase diagrams that we will come to. If you don't do the optimization, you will make totally wrong conclusions about the phase diagram. So that brings us to the phase diagram. And let me look at the chat. No, still silent. So it's still silent. There. So the phase diagram is something that several people explicitly liked, but other people also explicitly thought, well, I don't really see the value of this. I don't get it why we spend so much time to phase diagrams. Well, let me try to bring their value across. Yeah, the procedure first. So how to, we did a small calculation. What would be the formation energy. So the energy difference between the elemental crystals, FCC aluminum, BCC iron, and the alloys in two different crystal structures in our orthorhombic crystal structure or in the C-subchloride crystal structures. So let's, the formation energy the difference between the alloy and the elemental crystals and the larger this difference is the more negative this difference is the more stable the alloy will be and if people did the calculation then where is the result yeah the result is here then for the orthorhombic crystal it's something like minus 0.15 electron volts for the caesium chloride structure it's minus 0.30 so much lower someone else found minus 0.06 for the orthorhombic minus 0.30 for the caesium chloride yeah it depends a bit where you start from do you take the fully optimized crystal or one of the intermediate values so there can be a bit of need for a more stable crystal so it depends a bit on the value of the orthorhombic crystal numerical scatter on these numbers, but the overall picture is clear that the cesium chloride has an energy, a formation energy, that is lower than the formation energy of the orthorhombic crystal. And therefore, if we look at the phase diagram, if the cesium chloride iron-aluminum is here, at about minus 0.30 eV per atom, then our iron-aluminum orthorhombic crystal will have energies that are much higher. Depending on which optimization we did, the one, our ideal starting configuration, had a positive formation energy, and the more we optimize, up to the full optimization, we get a negative value, but in all cases, a value that is not as negative as the one for the cesium chloride structure. Now, maybe I should first show, this is indeed something that you have found as well, so these are some screenshots from your report, and this is a breakdown in the different steps with numbers. But I go back to the previous slide. I go back to this picture of the phase diagram, because I want to draw your attention to a few things you can do with this. So first of all, was it important to do the geometry optimization? Yes, because our initial guess had an energy that was really far away from the actual value. If we don't do the full optimization, we have no realistic idea about the actual value. In other cases, you could maybe go from here to much deeper, or, well, a lot is possible. Second, what can you learn from this phase diagram? Why is this useful? Well, we are searching for this green set of lines, which is the convex hull, so you make straight line connections between these two lines. So, you have to make a straight line connection between the two lines, and you have to calculate these formation energies for many different iron-aluminum alloys. In principle, there can be hundreds of thousands of possibilities here. And you make the geometric construction, where you have straight lines connecting the outer points, such that no further data point is under these lines. Well, these crystals, that are on the convex hull, are the ones that are thermodynamically stable. So, this is a quick way to find the relevant crystals from the big set of possibilities. And if you now take a crystal that is not on the convex hull, like this iron-5, aluminum-8, then, in the thermodynamic limit, this area is going to be less than, or better. So, you have to make a straight line connection between the two lines. Well, these crystals, that are on the convex hull, are the ones that are thermodynamically crystal will try to decompose into the two stable crystals to its left and right. So you look at which interval, at which segment this is, so here it is the segment between iron-aluminum-2 and iron-aluminum, and you know if you give this crystal an infinite amount of time, so to go to the thermodynamic limit, it will disintegrate into a fraction iron-aluminum-2 and a fraction iron-aluminum, with the right weights such that the stoichiometry is not changed. So this phase diagram gives you a hint for decomposition reactions. Okay, this was compared to materials projects where you see that the phase diagram is changed, and so you have a hint for decomposition reactions. And this was compared to materials projects where you see that materials project does not have all phases available so this is a limitation you have to be aware of if you use these databases try to check several ones because not every database has all information and well I want to come back here to the phase diagram what you can do with the phase diagram once you have these phase diagrams and the databases they show you the phase diagrams for certainly binary systems and in many cases also for higher dimensions for more elements so once you have these phase diagrams they can very much speed up the calculations you need to do for new crystals so let's take a hypothetical example, you have a ternary system with gallium, palladium and ruthenium atoms, and somebody gives you a unit cell, a guess of a unit cell, for that stoichiometry that is there on the screen. Gallium, palladium 3, ruthenium 2. Is that crystal stable or not? If you have no phase diagram information, then the only thing you can do is, you can calculate its total energy. You can maybe compare that total energy to the total energies of unary elemental gallium, elemental palladium, elemental ruthenium, and conclude whether that crystal is more or less stable. than this sum of elemental crystals. Yes, fair enough, but maybe there is somewhere a very stable gallium-palladium alloy, and that crystal will want to disintegrate into that gallium-palladium alloy, and remaining contributions of elemental palladium and elemental ruthenium. If you don't know that that gallium-palladium alloy exists, then you cannot make any meaningful conclusion. But how can you know that it exists? Do you really have to try out all possible mixtures of gallium-palladium and ruthenium? That would be an enormous work. And no, you don't have to do that. You can look at the phase diagrams in the databases. So what would be the steps you have to do? You get that hypothetical crystal structure with these elements. You do, of course, convergence testing. Then, once you know how to get reliable total energies and forces, you do the full geometry optimization. And then you go to the databases. For instance, the OQMD, which is very powerful for phase diagrams. And in the OQMD, you take this GCLP algorithm, and you fill out there the composition, so not the crystal structure, the composition of the crystal you are examining. And OQMD will compare that stoichiometry to all the crystals it knows about. And it will tell you, well, for all the crystals I have in my database, the most stable, the most stable situation is to realize that stoichiometry is if I take twice, twice the unit cell of elemental ruthenium, 0.4 times the unit cell of elemental palladium, and 0.2 times the unit cell of gallium-5-palladium-13. That crystal itself was clearly just a structure of the higher-equation electron. So, I have well is not on a convex hull otherwise there would have been no decomposition you would have seen here just one time the unit cell of that ternary crystal so but now you know that the best known competitors are these three crystals so you do a calculation now using the same settings as the ones you used for your ternary crystal calculation you use the same settings to calculate the total total energy of the ruthenium crystal the palladium crystal and the gallium-5 palladium-13 crystal so three additional calculations with full geometry optimization and now you make the weighted the weighted average of total energies in this way and this will be the total energy of the ternary crystal and this will be the total energy of the ternary crystal and this will be the predicted total energy of this decomposition which you then can compare with the total energy you have just calculated for the ternary alloy and you will see whether that ternary alloy is more or less stable than this decomposition so thanks to the phase diagram with a targeted calculation of a few relevant phases namely the ones that are suggested in this diagram and the ones that are suggested by OQMD you can make a conclusive statement about stability of that complex crystal or or whether it is not stable at all and without the help of the phase diagrams you would be totally in the dark there so phase diagrams are really a powerful tool it's a way to save our energy and energy for later generations because every crystal every data point adds something to the phase diagram and the phase diagram is the ultimate summary of everything we know about this about this set of elements binary ternary or more okay by this we have reached the end of the scientific parts let's have a brief look at next week next week will be about electronic structure so we go away from the geometry in three-dimensional normal space and we will think about properties that depends on the energies of the electron bands and we will learn to calculate the electronic structure plots of these blocks or quantum blocks to be exemple encoded in lot testament programs a crystal, the band structure and the corresponding density of states. And as usual I ask you to write a summary in a few lines about the past week, what are the most essential things you surely should remember about this, and what is one or more good exam question that could be asked about the content of the past week. So five minutes for this, and afterwards I will have a last look at the chat. Okay, thanks for your contributions. So let's have a last look at the chat. I see nothing there, so that means we can stop here, and I'll see you again next week, same place, same time, for the evaluation. electronic structure topic. Bye bye!