

## Computational Materials Physics (2023-11-20)

### Week 8 : chemical bond

*(automated transcription)*

This is the feedback webinar on the topic of the chemical bond and just as last week this one is pre-recorded. This time even without having seen all reports. So I looked at the reports that had arrived until Friday afternoon. In case you have questions that you asked and that was before Friday afternoon, then I will not have seen them, but such questions will then be dealt with in the next webinar. All questions that were asked before Friday afternoon will be covered. About the project, the reports that I have received show that all the teams are still going fine. By the time you hear this feedback webinar, all teams should have received that feedback already. But I will not say anything further about the content of that feedback here. There were a few questions about particular tricks that could help to make your calculation work more comfortable. I have summarized this here in a list together with some questions that were asked in previous years. What follows the following minutes can be useful to make it more convenient to run your calculations or to solve some errors. Somebody asked is it possible to save time by starting a new calculation from the output of a previous one. Like you have run a calculation with a certain basis set size and now you want to continue with a larger basis set size. But rather than starting from the very first point again, can't I start from my converged density of the previous calculation. That would probably save you a few iteration steps. And the answer is yes, you can do that if you introduce these two red lines in your electron block. And if you use for your second calculation the same prefix value as for your first calculation. So that is relatively straight forward. The opposite question is can I stop or pause a calculation and then resume it later. And here you see how you can do that. So on the command line you give the command touch. Then the prefix value that you used in that calculation followed by .exit in capital letters. And at first nothing will happen. But the next time your calculation will want to start a new iteration then it will stop in a clean way. If you then in the input file add this line restart mode equals restart in the control block. And you submit that input file with exactly the same pw.x command as before. Then the calculation will restart from that point. A bit of a more rough way or less elegant way to do the same is just to pause your virtual machine. If that is sufficient for your purpose. If you close the virtual machine it will ask you do you want to really stop it or do you want to let it hibernate or sleep in this situation. Well if you choose for sleep then it will save your current status of the machine to disk. And next time when you reopen the virtual machine it will continue from there. And your normal laptop will be free meanwhile to do whatever else. So that is also a possibility. But if you do it as given here on this slide then your virtual machine is free and you can do other things on the virtual machine. So it is up to you what exactly you want to do. What can also be useful is knowing how to run a magnetic or spin polarized calculation. We didn't really touch that topic yet. But if for the project you would want to do this. The procedure is add in the system block the keyword nspin equals 2. And then add as many lines as you have atoms. So here you have ntip equals 2. That means you have to add 2 lines with starting magnetization. With an index 1, 2 that just counts until ntip. And that starting magnetization can have the value 1 all the time. That is not a problem. So for a simple ferromagnetic situation this recipe will work. We will deal with magnetism later but this is a quick start. And the effects of a magnetic calculation that you see at this place in the output file. You will find magnetic moments for every atom. This here in this example with 5 atoms. There are 3 atoms with a magnetic moment of a bit more than 2 Bohr Magnetons. Atom number 4 has a magnetic moment in the opposite direction of minus 0.2 Bohr Magnetons. And atom number 5 has almost no magnetic moment 0.039 Bohr Magnetons. And you also get the total magnetization in the entire cell. An error that sometimes appears is that your calculation stops and the only thing you see on the command line is a killed message. If that happens it probably means that you try to run something for which your virtual machine does not have enough memory. So not storage space on disk but active memory, RAM memory. And to see whether or not that is the case look somewhere in the beginning of your output

file. There is a line estimated total dynamical RAM. And in this example here that is 3.9 GB. And then go to VirtualBox, go to settings and check the memory that you can actually use. I will show this on the next slide. So in VirtualBox while Quantum Mobile is running go to settings. And look in system, motherboard and there you have in the first line base memory that is indicating how much you can use. In this example here 10 GB. So that would be sufficient to run a case with 3.9 GB. But if you see that it is only at 2 GB then you can change it here. If I remember it correctly you cannot change it while Quantum Mobile is running. So in that case you will have to stop Quantum Mobile first, then change the memory and then restart it again. So far the list with some hints for making your computational life easier. Sorry if I have to cough every now and then. I am not ill anymore but still some leftovers in that coughing. Good, chemical bonds. That was the topic of the past week. And how does that fit in the entire story? I told you last week that at this stage we have finished part of the course where we give some input, volume, shape of the unit cell and positions within the unit cell. We used that to calculate total energies and we derived properties from this. The equilibrium volume up to the phase diagram. And then in the week before the present one we increased the number of properties that we could calculate by looking at band structure and density of states. A topic from condensed matter physics from which we are able to predict other properties. We did not go into detail predicting the color or predicting spectroscopic properties. We did not actively do but in principle that is possible based on the band structure and density of states. We did learn how to recognize whether our crystal is a metal or an insulator. In the present week, the week you have just finished, we take information that is more of a chemical nature. So we will calculate the electron density, visualize the electron density and that will give us some qualitative insight in the chemical bonds. And therefore we first looked at chemical bonds as they are commonly described in textbooks. We distinguished the ionic bond, the covalent bond, the van der Waals bond and the metallic bond. We reviewed some properties that in textbooks are associated to each of these types of bonds. One of those properties was that covalent bonding leads to crystals that are rather brittle. That can lead to the question, especially among materials engineers, what has covalent bonding to do with brittleness? Materials engineers think about other properties when they deal with brittleness. First of all, covalent bonds introduce directionality in the bonding. Therefore you can expect that if you try to modify a crystal, if you put stress on a crystal in one direction, say perpendicular to the bond or parallel to the bond, that this gives differences, that there is an anisotropy in the reaction of the crystal. And that will often lead to brittle behavior in one direction. Shearing a crystal in one direction might lead to an easier breaking of the crystal than in another direction. So at that level covalent bonding is related to brittleness. But there is also another level, the level of microstructure, the level of defects in a crystal, and interaction between defects in a crystal that also leads to an increase or decrease of brittleness. The typical example is a dislocation, a half plane of atoms that is inserted in an otherwise perfect crystal. Wait, let me move to the pointer. You see this here, this is a half infinite plane of atoms that is squeezed into these other infinite planes of atoms. And if you now try to shear this crystal, say you push here at the top to the right while you keep the bottom fixed, then it will break and restore some bonds here in that region, which effectively has the result that a new plane becomes the defect plane, and then again a new plane, and so on. So the net effect is that you move that half infinite plane through this crystal. And such a moving dislocation will avoid that the entire crystal breaks. So you will have a crystal that is less brittle thanks to that defect. So a perfect crystal here could be brittle because if you shear, in the end you have to break the bonds. If you have that defect, you will move the defect through the crystal and the crystal will not break. So that is brittleness or ductility, the opposite of brittleness, at the level of microstructure. That is not the level we are focused on in the first place in this course. We look at properties of more or less perfect crystals. But if you have a materials engineering background, then this might help to put the things in the proper context. We looked at cohesive energies, and I asked you a question that sounds like a textbook question from a solid state book or a solid state chemistry book. And that question was meant to make the connection to these more macroscopic properties in solid state chemistry. A cohesive energy, working with a cohesive energy, is something you might meet in other contexts. And here I wanted to show that this is a property, you can compute it from DFT. But once you know that, you can do macroscopic things with

them. You can determine how much energy is released when a reaction happens. And this translates in what was asked here, how much the room would heat up. Well, how much will a room heat up if you mix a teaspoon of free sodium atoms with a teaspoon of free chlorine atoms? And these are some of the answers you submitted. They are, I would say, somewhat spanning a large range, from 0.4 Kelvin to more than 100.000 Kelvin. And you have received the feedback document. And you have seen, if you submitted your answer, then you could immediately download a document with the correct reasoning explained. And there you will have seen that order of magnitude a few Kelvin is the right answer. So probably all these answers from 0.4 to 5 Kelvin, they are OK. And the reason why they are different is, well, this was a question where you had to make quite some assumptions. How large is the room, for instance? And depending on which assumptions you made, your answer can be a bit different. If you have values that are considerably larger, like the last two in this list, then you need to revisit what went wrong. In any case, a temperature increase of a few degrees, that's sizable. If you have just two teaspoons of ingredients, you mix them and you get that increase in temperature, that is a large effect. And with this I wanted to illustrate that cohesive energies of normal crystals, that these represent really large energies. To get a feeling for these numbers. Someone asks, I hesitate what is the difference between the cohesive energy, what we saw this week, and the formation energy that we discussed in the week before, when it was about phase diagrams. And indeed it's important to distinguish these two concepts. It's just a matter of definition. A cohesive energy, that is by definition the energy difference between a crystal, a crystal made out of more than one element, like our rock salt crystal, and at the other hand, at the other side of the balance, the free atoms that constitute that crystal. While a formation energy is the energy difference between our crystal at one hand, at the right hand side, and the elements that make our crystal, but in their ground state. So the sodium, for sodium we don't take the sodium free atom, but sodium in its crystalline ground state, in sodium metal. And for chlorine, we take not the chlorine free atom, but the chlorine diatomic molecule, and then one half of that, because we want values per atom. So you could calculate once and for all, what is the energy difference between the sodium free atom and the sodium elemental crystal, and the same for chlorine and the chlorine molecule, and once you know these numbers, you can always convert formation energies into cohesive energies. Depending on what you want to do, sometimes one is more convenient than the other, so it's just a matter of definition. Now having this concept of cohesive energy, and what we then introduce thereafter, charge density differences, with these two ingredients we will look what density functional theory can tell us about chemical bonding. First we need to be able to calculate cohesive energies, you tried that, and somebody asked, well in two different ways, I don't understand how to calculate the energy of a free atom with DFT. I gave you the ingredients for that, but I agree that at this point we didn't discuss this in detail. So I gave you a few input files, a structure input file, and a corresponding pseudopotential, just with the message, if you run these through quantum espresso, you will get the energy of the free atom. Now what did you actually do, what is in that input file? If you visualize the input file, you see that it looks like there at the right hand side, and that's for the case of aluminum, for all of these cases, this is a primitive cell for an FCC lattice. And if we start measuring distances in that FCC lattice, so I measure the distance between this atom in yellow here, and this atom in yellow here, then you see that they are more than 10 angstroms apart, that's very large. This is not the unit cell for a crystal, this is a very artificial situation. I have two atoms that are so far away that they effectively don't feel each other anymore. Why is that? We have quantum espresso, a code that is meant to calculate properties of crystals. It always needs an input file that is a unit cell, but here we need energies for free atoms. Well, our trick is, give an input that formally looks like a unit cell for a crystal, this is an FCC unit cell, but make the lattice parameter so large that the atoms are far apart from each other and don't feel each other anymore. So the energy that you calculate will be effectively the energy for a free atom. We will deal with supercells in one of the coming weeks, and then this will be explained a bit more systematically, but I hope that at this point you get at least that part of the concept. This is a rather expensive way of calculating free atoms, because a large cell with a lot of vacuum, that is expensive for a DFT calculation with a plane wave basis. And there are DFT codes that do it in different ways, that have solvers that can also work in zero dimensions, so that can do a free atom, not in a

supercell, but really in infinite space. That's possible, but quantum espresso does not have this. So this is the same question formulated in a different way. It was in this way that it appeared in the form, I think, for cohesive energy. I felt that I could reproduce the input files for the crystals, but not the ones for the single atoms. And I'm not sure that we discussed this in the course already. So yes, that's true, we didn't discuss it yet. At this stage, these input files are just to be taken as a given, but once we have discussed supercells, you will fully understand what is in there. And with the explanations of the past few minutes, you understand maybe already now what is in there. Someone else noticed that if you look in these input files, that there is always  $n\text{-spin equals } 2$ . So these are input files for magnetic calculations. Whereas the crystal calculations for FCC aluminum, for instance, they are non-magnetic. Why is that? The reason is that many free atoms are magnetic. If you look in the periodic table, and you look for instance at aluminum, it has one electron in its p-shell. So according to Hund's rules, that must be an unpaired electron. And therefore, a free aluminum atom will have a magnetic moment. And if you want to reproduce that with DFT, then you need an  $n\text{-spin equals } 2$ . You need a magnetic calculation. If you would make crystalline aluminum, FCC aluminum, then magnetism will be destroyed. And if you would do the calculation with  $n\text{-spin equals } 2$ , you would very likely find at the end of your SEF cycle that there is no magnetism left. But if you know this already in advance, that this will happen, and for most solids that do not contain one of the typically magnetic elements like chromium, manganese, iron, cobalt or nickel, for most crystals you know that they will not be magnetic, so therefore it's no use to use  $n\text{-spin equals } 2$ . You can immediately put  $n\text{-spin equals } 1$ , which will not allow for any magnetism, and which will lead to a faster calculation. But for the free atoms, unless you have completely filled or half-filled shells, no, sorry, not half-filled shells, unless you have completely filled shells, then you must switch on the magnetism. With the data you were given, you were able to complete this table, and there was also a link to the table in the course, so you have seen this table. And if you didn't succeed to reproduce at first try the numbers, the cohesive energies here, well, then it was because you were not subtracting the right amount of atoms from each other. And so it's very important if you do such exercises that the energies of the free atoms, and these are the ones here, and the energy of the crystal, that this is for the same number of atoms. So if you would count the number of atoms and the number of different elements here, that must be exactly the same as the number of elements here at the right-hand side. So in this case here, this is 1 chlorine atom and 1 sodium atom, and the energy you have here is the energy for 1 formula unit of rock salt, so for effectively 1 chlorine atom and 1 sodium atom. And that leads to 6.2 electron volts per unit cell, because a primitive unit cell contains 1 formula unit here, nor if you express it per atom, because there are 2 atoms in the cell, so it's 1 half of this, it's 3.1 electron volts per atom. So most mistakes are always due to not making this balance correctly. Subtract the same number of atoms from each other. Should you do a geometry optimization when you want to calculate the total energy of the crystal, for which you want to calculate the cohesive energy? Yes, definitely yes. And you could see this from what we found last week. If I start from this ideal stacking of spheres, and if I would give you that crystal and I ask you to calculate from this one the cohesive energy, well if you wouldn't have done the volume optimization or the geometry optimization, then you would have, well here it's for formation energies, you would have found a positive formation energy. It's only when you do the full geometry optimization that you find a strongly negative formation energy. And formation energies and cohesive energies are just a constant number apart from each other, so the same conclusion would help for the cohesive energies. Without a proper geometry optimization these numbers are not necessarily meaningful. Of course if you know already the experimental crystal structure, experimental lattice parameters, then probably you will not be too far off if you would do a static calculation for that experimental cell. So this was about cohesive energies, and we can distinguish at least the van der Waals crystals, so let me go back to this here. We can distinguish at least the ones that are van der Waals bonds from all the others, because these have cohesive energies that are very small. Now we want to find ways to distinguish also the other three types of chemical bonds from each other, and that is where we can use the charge density difference. So what do we see in a charge density difference? This is one cut through an FCC aluminum crystal, and what is visible here? We have the charge density of a superposition of three atoms, so at every position in the

crystal where we have an FCC aluminum atom, we put the density of a free atom, which is a three-dimensional object, and then we calculate the electron density for the actual FCC aluminum crystal, and this density and the superposition of free atom densities, they are subtracted from each other. Which one you subtract from which other one, that's a matter of definition. The two types of definition, atomic minus crystalline, or crystalline minus atomic, they are both used in the literature. What is used here is the one that leads to, well, where the purple regions are regions where electrons move to in the crystal. So in the, let me say that again, so I search for regions where we have this deep purple, and that is here in between the aluminum atoms, so these are regions where there are less electrons in the superposition of free atoms than there are in the real crystalline density. So when you bring these free atoms together, some electrons will move to this purple region, and the blue region is the region where exactly the opposite happens, so electrons move away from here. So what we see here is a rather spherical density, and electrons accumulate rather homogeneously in the region in between the atoms, so that is what you expect for a metallic bond, and not surprisingly you see this for FCC aluminum, something that definitely is a metal. If you would do the same for germanium, a semiconductor with strong covalent bonds, then you see that you find these purple regions, here always in between two germanium atoms, so not spherically distributed, but rather anisotropically distributed. In the germanium-germanium region, so in the halfway to germanium atoms, there you have an accumulation of electrons. So these bonds are not isotropic, they are anisotropic, and that is typical for a covalent bonding. And finally for rock salt, there we see the accumulation, the purple region, around the chlorine atoms. So apparently here charge accumulates on the chlorine atom, and at least there is not such a strong charge accumulation around the sodium atom. And this charge transfer from one atom to the other, that is typical for an ionic bond. So by inspecting these pictures, you can understand what these typical textbook types of bonding are. The historical difference is that the people who constructed these concepts, did that based on experimental information. We used a DFT calculation, more in particular the charge density difference plot from a DFT calculation, and made the assignments of bonds based on that. Two different routes, but they are consistent with each other. A practical problem that sometimes might appear at this stage, when you want to calculate these charge difference density plots, and you want to, in that process, some people do not find the submit button. If that happens, that is because there is something in the configuration of your quantum mobile, that needs to be updated. So within quantum mobile, not within VirtualBox, really within quantum mobile, you have to open the settings window, take displays, choose resolution, and then change the resolution to a different value. Because if you didn't see the button, as it is here on this screen, the button should be here at the bottom, but it's not there. That is because the resolution is not set right. If you make a different resolution, then this window will shrink, and you will see the buttons you need. Somebody asked in the forum, this charge density minus superposition of atomic densities, how is that actually calculated? Because we calculate only the charge density for the crystal, and we never actively calculate the charge density for the free atoms, in contrast to what happened there for that cohesive energy calculation, where we had really files for the atoms, but these ones we didn't need here. So how is this calculated? Well, a free atom for DFT is a very quick thing to do, if you do it in zero dimensions, so really one atom in infinite space, and Quantum Espresso can do that internally. So if you ask for a charge density difference, it will do your regular crystal calculation, but then will internally calculate the densities for the free atoms, which is a very quick job, and will then put these densities at the same positions in your crystal, where you have in this case the aluminum atoms for instance, and do the subtraction. So you don't have to manually calculate these free atom densities yourself. And so with this you should be able to tell, or to analyze chemical bonds in a crystal based on DFT information. In order to understand crystal orbitals, and chemical bonds from a somewhat different perspective, there was this topic which was called an old puzzle, and that actually went back to something I asked you in one of the earlier weeks. In one of the earlier weeks I asked you, how is the chemical bonding in rock salt actually happening, what have you learned about that in your previous chemistry courses, maybe even in secondary school. Can you make a picture that summarizes this, and we will use it later. You didn't know at that stage what that picture was meant

for, but now here I can look at some of the pictures you submitted. And this is one here where you see that there is an electron transfer from the sodium atom to the chlorine atom, in order to fill the shell of the chlorine atom, and to empty the valence shell of the sodium atom. And that makes then the chlorine atom negatively charged, and the sodium atom positively charged, after which these atoms will electrostatically attract each other, and you can form a strongly bonded crystal. Other things you submitted are pictures where this transfer of a single electron from one to the other is clearly indicated. These are indeed the textbook ways how people think about this ionic type of bond. But in the video you saw last week, you hopefully understood that this is not what happens in reality. If you look what happens with the real wave functions for these two elements, then there is not a jump from a sodium 3s atom to chlorine. No, rather if you look at the charge density around the sodium atom, then there is a peak in the charge density. Most of that sodium 3s electron is at this particular distance from the sodium nucleus, and the sodium chloride crystal, the rock salt crystal, will get established because that sodium density will want to overlap with the chlorine atom. So it's not a jump from sodium to chlorine, it's rather you have a natural distance from the s electron of sodium to the sodium nucleus, and that electron will want to overlap with the chlorine atom, so they will somehow hook into each other, and they will preserve that distance that is dictated by the 3s wave function. So this is a better picture to understand such an ionic bond than the picture of an electron jump. That was the message of that video on the old puzzle. And in all the pictures you contributed a few weeks ago, there was perhaps one that expresses this idea correctly. I don't know whether that was consciously done by the author of that picture, but at least in this picture you cannot tell that they have the idea of a jump. You could think that this electron here was a 3s electron from sodium that fills the hole in this orbital of chlorine with 7 electrons, due to which there is a de facto negative average charge in the chlorine region, and a positive actual charge in the region of the sodium atom. We also used rock salt to talk about crystal orbitals, and somebody asked here how can we plot with quantum espresso these orbitals in x-cris then that correspond to a particular k-point and band index. I'm not sure whether that is possible in quantum espresso. It may be, it may be that it is not possible, I don't know. I never really tested this, because these pictures were made long ago in another DFT code, in Win2k. There this was pretty straightforward, and it's not the goal that you are able to calculate such pictures yourself. This was just meant to illustrate the concept of crystal orbitals, but if you want to do them, neither we should find out how to do that in quantum espresso, nor you use the Win2k code. This here was a summary of what we got there. If you take a 1s orbital, which would be in the band structure deep down here, it's not plotted, then you would find contributions that are each very much localized around one atom. If you plot the 3s orbitals, then you will find regions that are delocalized over space, that span all atoms of the crystal. So these orbitals, they are effectively crystalline, well, all of these are crystalline orbitals, but some are localized around one atom, and some are delocalized and span multiple atoms. Therefore, an electron in that orbital can move throughout the crystal. It is not bound to one particular atom. So far, the feedback on the chemical bonding topic. Should there be questions left that you asked before submitting your report, but after Friday afternoon, well, then I will not have seen them, because I recorded this video before that moment, but you can still put them either on Zulip or in the forum, and I will deal then with them in the feedback webinar of next week. In the week that lies in front of us, we will deal now with a topic that is more from materials engineering, namely we will learn to calculate elastic properties of solids. We have had already this a little bit with the bulk modulus, which is a famous elastic modulus of a crystal, but we will go now in much more detail about this, and we'll calculate basically all elastic properties of a crystal. You have now the possibility to write as usual a summary about the past week, just a few lines, and to formulate a corresponding exam question. I will not let this run during five minutes. You have the link to the forum here, so please do this and submit it, and with this we are done. As this is not live, I cannot look at the questions you have now currently live, but again, if you still are left with questions, put them in the forum, put them in the question forum, put them on Zulip, wherever, and I will deal with them next week. Bye bye.