

Computational Materials Physics (2024)

webinar 03 – Density Functional Theory, part 2

Today is the second webinar on density functional theory, a big topic, therefore split over two weeks. But as usual, before going to the science, let's do some housekeeping. And what are the housekeeping messages for this week? There are three project teams formed. So there were several people who preferred the final exam rather than the project. In previous years it was the other way around, but that's fine. So therefore only three project teams. I didn't inform these teams yet, I will do that right after this webinar. So you can expect a mail in the next one or two hours. And for the project teams, the different issues. Intermediate dates are as announced long before in the general time outline for the course. So next week a work plan is requested. And that can be in broad terms, you don't need a very detailed work plan. But at least a vision on how you plan to tackle this project. Such that you are motivated to start working and not postponing. Until two weeks before the due date. On November 10 there is a first intermediate report. Where I ask you to write down a short status on how your work is proceeding. And to show the convergence tests for your crystals. And that's important. You have seen or will see soon what convergence tests are. And for the project it's important that we can verify early on whether your convergence test is sufficient. Otherwise you risk to do calculations for the rest of your project that are not meaningful. And then on December 8 the final paper and the final video of the project are due. Just a warning in case chemistry students. So students from the... Master of Chemistry of Ghent University would see this video. For them they have a separate version of this course. And for them the timeline and the content of the project is different. So they should just neglect what is on this page. Just in order not to confuse them. I have also seen that in many forum contributions. This was clearly not written. By a student but by ChatGPT. And I'm a bit well puzzled by that. I like ChatGPT and similar tools. I use it a lot. Multiple times a day. But it's increasingly clear that there are productive uses and unproductive uses. And using ChatGPT or a similar chatbot. Just to... Populate the forum. And to clear your... To check your box. I have done the work for this forum. That's really unproductive. You will have noticed by now that the questions that should be discussed in the forum. Are meant to trigger some misconceptions. And by discussing in these feedback webinars. The misconceptions that you show. Well, all of us learn. If, however, everybody would ask ChatGPT to answer on the forum in your place. Then we will have 10, 20 basically identical answers. With maybe 20 times the same misconception. Or without misconception. So, what is left to discuss. What is left to learn. That will not help us. It doesn't help you. It doesn't help anybody else in the course. There is a good reason. Why? For... Why these four points for doing the effort. Throughout the term. That this is really grading the effort. And not the content. So, you are allowed to make mistakes in these posts. It's from these mistakes that all of us learn. If you find the short answer. If you find the short answer. Where a computer program answers in your place. Well, whether or not the computer program is right. It will not help your learning. And it will also not inspire the others in the course. So, probably I will have to find another way to organize these forums. Or to replace them by something else. Because that is the reality in which we live. Tools like ChatGPT will never go away. And the challenge for us will be. How can we keep on learning. Even with these tools being present. They should help our learning. And not hinder our learning. But for the time being. It's still with the good old forums. So, I can only ask you. Answer yourself. Don't use chatbots. About Zulip. So, last week somebody asked to send a test message. In the administrative news stream. To check whether you receive an email copy of this or not. If you have configured it such that it should send you an email copy. So, I've done that. And also 10 minutes before. This webinar started. I've sent another message. So called to announce the webinar. So, you have two ways to check. Whether you received this as an email or not. Or whether it got in your spam folder. Or whatever. Or maybe you didn't configure it correctly. Such that it wasn't supposed to send you an email. Well, hopefully with this test. You can figure out how the status is for you. Thank you. And the last part of the housekeeping. After the first week. I asked for your mood about the course. What is the emotion that you would associate after

one week of studying. And these were the answers I received back then. I didn't show them to you yet. So, the first block in green are positive emotions. Then the intermediate block in yellow are rather neutral. Rather neutral emotions. And the lower block in red are rather negative emotions. So, that was the status after week one. Mainly positive emotions. And so this week, after week three. I asked you the same. And let's see how the evolution is. Still mainly positive emotions. Which is of course something I am happy to do. But I don't know. I am happy to observe. But a bit more of the neutral emotions. And in particular bored and impatient are increasing a bit. So, for a few people. This is perhaps going too slowly. Which I can imagine. If you have already some kind of background in this area. Then the start is a bit slowly. I expect that we'll feel differently. As the weeks proceed. But, yeah. It's a consequence of trying to get everybody on board. So the start needs to be a bit slowly. That's it for the housekeeping. Let's jump into the science. The second part of density functional theory. Where we looked in the first place to the two theorems. That are the foundation of density functional theory. The two Hohenberg cone theorems. And the first theorem we looked at. The first Hohenberg cone theorem. Was basically telling us. That there is a one to one correspondence. Between the ground state density. Of a many electron system. And the external potential. That defines that electron system. So if you know the density. You can in principle reconstruct the potential. And if you know the potential. You can in principle find the density. They are one on one. Connected to each other. That's what the theorem tells. It's a mathematical theorem. It can be proven. So this is absolutely true. And it has consequences. Because we are used to calculate properties. In quantum physics. By a bracket operation. On a wave function. With a wave function. And an operator. So you take the operator. O hat in this notation. That is corresponding to a property. And you sandwich it. Between the wave function of the system. And the result of that operation. Is the value of that property. That's familiar from quantum physics. But due to the first Hohenberg cone theorem. You can formulate this in another way. You can also say. There exists a functional. If you plug in the density function. Then it will give you the value of the property. That is because. There is this one to one correspondence. On this slide. And here I asked you in a forum. Go to. The DFT entry in Wikipedia. Or another encyclopedia. Read what is written there about DFT. And in particular about the first Hohenberg cone theorem. And compare that with what you saw in the video. Are there similarities and differences? And most people answered something like this. Like in the video we have seen this one to one correspondence. And on Wikipedia. This is discussed in slightly different words. With a specific addition that I will come to in a few slides. But basically it's the same. Two somewhat different points of view. To discuss the same. I will continue with that in a few slides. But I will first focus on a question. That has not been asked this year. But that has. Several times been asked in the previous years. And it's a question that is instructive. So let's read it. The first Hohenberg cone theorem. Specifically refers to the ground state. The density in that theorem is the ground state density. Does this mean that there is information about excited states. That is captured by the wave function. But is not present in the density. Should we still really need the wave functions. To describe the excited states. And are the densities just okay for the ground states. Or is that perhaps not true. And are wave functions really nowhere needed. Can we find everything based on the density. It's normal to ask this at this stage. And let's go through a reasoning that answers this question. We start from the density. The ground state density. We know. Due to the first Hohenberg cone theorem. That you can connect an external potential to this. Uniquely. There is only one external potential. Possible for a given density. If you know the external potential. Well that's the only crystal specific. Or molecule specific part of the Hamiltonian. So knowing the external potential. You can write down the entire Hamiltonian. Knowing the entire Hamiltonian. You can write down the Schrödinger equation. And in principle solve the Schrödinger equation. And you find the ground state wave function. Ψ_{ground} . And the ground state energy E_{ground} . No doubt about that. Everything here is about the ground state. So this is a direct consequence. Of the first Hohenberg cone theorem. However. Once you have the wave function. You can not only find the ground state wave function. You can also find the first excited state wave function. That's also a solution of the same Schrödinger equation. And the corresponding energy. The energy of

the first excited state. Is an eigenvalue. And you can do that for the second excited state. And so on. So what do we have here? An uninterrupted chain. From the ground state density. To all excited state wave functions. And excited state energies. So that means that really. All information. Not only about the ground state. But about all excited states. Is implicitly contained in the ground state density. It doesn't mean that we have. The tools and the knowledge. To extract this information already now. From the ground state density. But in principle. Just following strict mathematical logic. This is possible. This information is in there. So to answer to the first part of this question. Yes wave functions are actually redundant. You can do everything with the density. And then the question continues. If densities are indeed sufficient. What is then the reason. Why we never learned this in basic introductory courses. About quantum mechanics. Why does everybody. Still speak about wave functions. And the answer to that. Lies in what we just mentioned. About the. The way how you get properties. How you compute properties. For every property. It is well known. What is the corresponding operator. There is a recipe. To construct an operator. For a property. And if you then have. A many body wave function. Or an approximation for it. You can evaluate. This expectation value. And you have. A prediction for that property. Thanks to. The first Hohenberg-Kohn theorem. We know that. There is also a functional. That can tell us. The same number. But we have no recipe. To create these functionals. So this is more. A matter of principle. We know that the functional is there. But we do not know. The functional itself. Except for. A few specific properties. Like for the total energy. There we have good approximations. Of that functional. So that is the reason. Why. A lot of quantum physics. Still revolves. Around wave functions. With wave functions. Compute properties. With densities. It is possible in principle. But often not in practice. I said in the beginning. There is bad use of. ChatGPT in the forums. But there are also people. Who use it in a good way. Somebody wrote this in the forum. I asked to ChatGPT. To explain the first. Hohenberg-Kohn theorem. And it said more or less. The things you have said. In the video. But it also added extra information. It said. The first Hohenberg-Kohn theorem. States that the ground state. Electron density. ρ of R . Of a many electron system. Uniquely determines. The external potential. V external. Up to. 0. I don't know how to determine. That additive constant. Good question. Really good. If you can use ChatGPT. To find gaps in your knowledge. And then ask that question. That is perfectly. Legitimate use. What about that constant? That constant. Doesn't matter. Indeed. The different potentials. That are. Different from each other. Only up to a constant. They will give you the same. Properties. And I can illustrate that. With classical physics. Because this is not a new concept. You have met this before. Take an object. A ball. And you hold it one meter. Above the floor. In a building with several. Several levels. So the distance between. This ball and the floor. Is say one meter. And now you hold. The same ball out of the window. At exactly the same height. And now. You see it's maybe. 10 meters above. The ground level. The ball is in its. Same state. But the potential energy. The gravitational potential energy. Of that ball. Depends on. What is your reference level. Do you take the floor. As the reference level. Or the ground. As the reference level. And these two reference levels. They differ by. A constant. You have to make a choice once. And then. All objects have a unique. Gravitational potential energy. With respect to that reference. It's the same. The external potential. We have chosen a reference. We have set the energy. Of the. Interaction between the nuclei. And the electrons. Is zero. Once the electrons and the nuclei. Are at infinite distances. From each other. In rest. That's our reference. But you don't need to take that reference. You could take a different convention. And then. The energies will be different. By a constant value. That will not. Affect properties. If you here try to compute. What is the speed of the ball. If it falls the distance. To the floor. For the two reference. Choices. You will find the same speed. So. Observable properties. Do not depend on that constant. For. I hope. That answers. This question. Again. I didn't see it this year. But usually. There are people who comment. That this first. Hohenberg-Kohn theorem. Is kind of shocking. And incredible. We are so used to wave functions. We think that for quantum physics. At first sight. Rather simple. 3D function. As the electron density. Also contains all information. Quite shocking. And. Also not asked this year. But quite a classic is. That first Hohenberg-Kohn theorem. Especially the proof. About it. This was an optional part of the course. But if you were interested. In the proof. Which is absolutely not a

difficult proof. To follow. It's also a very short proof. But you will see. In that proof. It is a proof that is valid. Only for non-degenerate ground states. So the logical question is. What then. If our system has a degenerate ground state. Is the Hohenberg-Kohn theorem. Then not valid anymore. The answer to that is. Yes it is valid. Only the proof is more complicated. So Hohenberg-Kohn theorem. First Hohenberg-Kohn theorem. Is really. A universally. True theorem. Let me look. At the chat. Before going to the second. Hohenberg-Kohn theorem. No questions there. So far. I will keep going there regularly. So please don't hold back. The second Hohenberg-Kohn theorem. Here I asked you. Somebody tells. That the second theorem. It looks like. A natural consequence. Of the first theorem. And not a separate. Independent theorem. Do you agree with that. And give your arguments. This illustrates. Also what I said in the beginning. The legitimate use of chat GPT. If you write your own thoughts. Then. Misconceptions will be revealed. And this is a nice example. This is not a chat GPT answer. This is an answer that one of you. Wrote down. Him or herself. It goes as follows. Physics is about minimizing. Some kind of cost function. Be it free energy. Be it action. Or anything else. It is no surprise. That the density of the ground state. Has the lowest energy. The first theorem states. That this ground state. Is unique. Which is also something. I would not find surprising. This student says. From general knowledge of physics. So I wouldn't really say. That this second theorem. Is a consequence of the first one. But I don't think it's worth. Giving this theorem. Our name. Or am I missing something. Great that you added. That last sentence. It shows that you have some doubt. And yes. You are missing something. We will come to that. I show here another answer. Where the same misconception. Is present. Formulated a bit differently. I have struck through. What is the most wrong parts. Due to the first. Theorem. We know that any other density. Than the ground state density. Should give a higher energy. Because of the one to one correspondence. That is not. What the first theorem tells. That first theorem only tells. That there is this one to one correspondence. It doesn't tell you. That the. Ground state energy. That the ground state density. Would give you the lowest. Possible value. Energy functional. What is the correct answer. We are used to think. In terms of wave functions. And for wave functions. Even in your introductory courses. Of quantum physics. As soon as you started to do some mathematical quantum physics. You have proven. The variational theorem. For the wave function. You have proven. That the wave function. That is the lowest. Energy solution. Of the Schrodinger equation. That that one. Is the ground state. So any other wave function. That is a solution. Of the Schrodinger equation. Must have a higher energy. That is very powerful. Because that tells you something. About how you can find. That ground state wave function. But that is valid. Only for wave functions. And Schrodinger equation. The second Hohenberg-Kohn theorem. Tells you. That the same applies. To densities. And the total energy functional. So the variational principle. To which we are familiar. Is true. For densities. The total energy functional. But we didn't know that. Before this theorem. Before we had proven this theorem. It looks like wave functions. And the Schrodinger equation. But you had to prove this once. For wave functions. And the Schrodinger equation. Maybe so long ago. That you already forgot. But that doesn't mean. That you can carry this over. To a totally different situation. Because we are working now. With densities. And a functional of the density. That returns us the total energy. We have to check. Whether or not the variational principle. Holds here. And the second theorem. That can be proven mathematically. Tells us it does. I will not read. These two other rather long answers. They are correct. So you can go back. To this video later. And read them for yourselves. Or to. Other correct answers. Formulated in a. More short way. I rather want to. Repeat this picture. That is a picture. That comes from the video. And that expresses in a cartoon like way. The total energy. Found by. Applying the. Energy functional. On the density. So this is some hypothetical. Density axis. And there could in principle. Before we have proven. The second Hohenberg-Kohn theorem. There could be two possibilities. The. Energy as a function. Of the density. Could look like this. Or could look like this. In both cases. You can draw in such a way. That the energy that is given. At the intersection. So for the ground state density. That that is the same energy. So it could in both situations. It could be perfectly possible. That plugging in. The ground state density. In that energy functional. Would give you the correct. Ground state energy. And the correct value. On the vertical axis. For this crossing

point. That can be realized. With either of these two types of curves. But the second theorem. Tells us. That it is the left hand side. That is the correct one. That this correct value. For the ground state energy. Is also the lowest possible value. That this energy functional. Can adopt. Which would not be true. In this situation. Here at the right hand side. So this is the variational theorem. But for densities. And energy functionals. I go. Again to the chat. Nothing there. Then we move on. To the Kohn-Sham equations. Another important concept in DFT. But not as fundamental. As the first and the second. Kohn theorems. These two theorems. They are really the foundation of DFT. You only call it DFT. If these two theorems. Are true. But then. You have different ways. How to do practical calculations. Within that framework. And the Kohn-Sham equations. They are one of these schemes. To do practical calculations. By far. The most important scheme. 99% of all DFT activity. Nowadays. Is with the Kohn-Sham equations. So. Often people consider this. As. It is DFT. Kohn-Sham equations is DFT. Strictly spoken it is not. In practice it is. And. In order to understand. The meaning of the Kohn-Sham equations. Better. I ask you. Apply the idea of DFT. To the solar system. Which is a gravitational. Many body system. And describe. How the different ingredients. Of DFT and the Kohn-Sham method. Would look like. In the solar system. And here I have an example. Of an answer. Where I am pretty sure. DFT generated. And that illustrates. That ChatGPT doesn't know. All physics correctly. It is telling here. You can apply DFT. To the solar system. And then rather than working. With electron densities. You will work with mass densities. And then it continues. Its explanation. Which is. I would say correct. The point of the comparison. The point where the comparison is difficult. Is. How do we compare. Electron densities. With these mass densities. In a gravitational context. I will show. In a few slides. What I mean by this. Another. ChatGPT answer. For the same question. Makes the same. Big step. To treat the mass density. ρ of R . Of the planets and the sun. In an analogous way. As the electron density in DFT. Yes. But if you try to do that. You will hit a problem. So I wanted to know. That was part of the purpose of this question. I wanted to know. What that problem was. And. In an answer. By a real student. You can see. A first hint. Of what the problem is. The answer is not complete. But at least it indicates that problem. Assume that the sun. Is the nucleus. And the planets are electrons. There are no coulomb interactions. But gravitational interactions. Between the planets and the sun. The planets have an. Exact orbit around the sun. Where exact means. That the location is known. We know at every moment. Where a planet is. And that is not the case. For electrons. Electrons have only a probability distribution. So that is. The big difference here. Or one of the two big differences. We will need to find a solution to this. If we want. To treat the solar system. In a DFT. Like way. And these are two answers. That come very close. In that respect. They tell. You could smear the planets. Over their orbits. Until you have a kind of. Time averaged orbits of the planet. Rather than having the planet. At one point in space. You can have it equally distributed. Over its orbits. Then you have really. A mass distribution. A continuous mass distribution. And that would be. A way to apply. A DFT like formalism. Now how would that look like. In a bit more detail. We have seen this slide. Where we have. The different groups of terms. In the actual Schrodinger equation. Electrons that move. With some kinetic energy. That are subject to the Coulomb interaction. Due to the nuclei. And that are Coulomb interacting. With the other electrons. This is the. True Hamiltonian. But we replace this. By a fictitious. System of particles. That are not interacting. With each other. There is no particle-particle interaction. So in the case of the solar system. There should be no. Planet-planet interaction. We have some magical. Mass. Some magical bodies with mass. That attract. Only the sun. And not any other of these. Bodies. These quasi-planets. They have kinetic. Energy. That's the first term. That you can identify. With the Koncham Hamiltonian. They also. Interact not with the. Immediate. Momentaneous position. Of the other planets. But with that time averaged. Smearred out position. Of the other planets. That's the equivalence of the Hartree term. That's why we needed to smear out. The planet over the entire orbit. They also. Interact with the sun. That's the equivalence of. Interacting with the nuclei. And then. Now you have made quite some approximations. You have neglected. The planet-planet interaction. You have smearred out. The planet over its orbit. And still we need a method. That gives us the exact solution. So we have to. Compensate for all the. Approximations that we made. And that is by. Introducing the

exchange. Correlation term. That somehow magically corrects. Everything that we have. Approximated. Which is of course. A dirty trick. This will only work if you have. A recipe to find that. Correction term. To find that exchange correlation functional. And that is where all the. Difficulty in DFT lies. But. The main part. Of asking you to think about. This gravitational problem. Is to reflect on. The meaning of these. Three groups of terms. In the Kohn-Sham equations. And to understand better. What they mean. There is also another aspect. That is different. And that is the second big difference. Between the solar system. And a quantum system. And that is the distinguishability. If you change two planets. You will notice that. If you interchange two electrons. That must by construction. Be unnoticeable. And that has some. Consequences. We will come to that in a few slides. Again a quick peek. On the chat. Nothing there. Then we continue with that. Exchange correlation functional. And. Here I asked you to read. A short article. A somewhat reflective article. A perspective article. From science. More than 20 years ago. About the search for. What is called. The divine exchange correlation functional. The absolutely true and correct. Exchange correlation functional. An object. That if we would know it. Then all of computational physics. Would be just. Run the computer. And get the correct answer. But we do not know it. And so. Part of the game is. Find better and better descriptions. Of this exchange correlation. Functional. And in that article. John Perdue. Of. There was presented. The Jacob's ladder analogy. By John Perdue. A kind of a. Community program. A guideline for the. Theoretical condensed matter community. To work on better and better. Exchange correlation functional. And they use this. Image to classify. The functional. According to five classes. The simplest one. The local density approximation. That only depends. So the contribution. To the exchange correlation. Of a given point. In space in a crystal. Only depends on the value. Of the electron density. At that same point in space. That is what. The local density approximation. Tells. A generalized gradient approximation. Takes. Additional information. That will also look. How the density varies. If you change that point in space. In the. Meta GGA's. They will also add information. About the kinetic energy density. At that same point. Not just the electron density. But the kinetic energy density. Of the electrons. In the. Hybrid functionals. There the exchange interaction. The exchange part. Of the functional will. Be exactly calculated. And that has. Some consequences. On what to do with the correlation. And then there is the class of the. Random phase approximations. Where you also will. Take into account. Unoccupied orbitals. So. Describing this by words. Is rather straight forward. Having this implemented. And having really functionals. At each of these five levels. That is not always so easy. And part of the difficulty. Is that. You need to. You will need to make approximations. And you will make approximations. In exchange. And in correlation. These two different contributions. To the functional. You will make approximations in both. And your functional. Will be a good one. Not if you keep the approximations. In both very small. Because that is probably. Even not possible. But if you can somehow. Manage it in such a way. That the mistakes. You make in the exchange part. Are largely cancelled. By the mistakes you make. In the correlation part. Then your functional will. Perform. Satisfactorily. And that is what a bit by chance. Happened already. For the local density approximation. It was expected. To be a very very rough. Approximation. But because it is the simplest thing you can do. Let's have a look at it. And then it turned out. That this local density approximation. Is not that bad. If we compare its predictions. With what we can measure. For real crystals. It is not that bad. Why is that? Because you have this error cancellation. Between the exchange and correlation part. And that you try to maintain. Through all the other. Rungs of the ladder. Somebody. Once made the comment. This looks a bit obvious. Do you need. A name for this? Do you need a story for that? And I agree. That this is probably. A bit of overkill. But. Everybody knows. These five classes. Of Jacob's ladder. And its great value. Is that it gave. A program to the community. To explore. Better and better functionals. You are not just walking in the jungle. Without a map. With Jacob's ladder. You had at least a rudimentary map. That outlines where you should go. And that led. To functionals. That were better and better. And it is worth mentioning. That in this context. A functional that is. Almost 10 years old now. And that became. Quite successful. The scan functional. Which was first published. In this paper. And I show you here the abstract. A very short abstract. That exactly tells. What this is about. It is a meta GGA. So

it is a functional from the third rung. Of the ladder. And the interesting thing is. Although we do not know. How the exact exchange. Correlation functional looks like. We can prove properties. Of that exact functional. And there are to date. 17 properties. Of that functional known. 17 mathematical statements. That this. Exact functional. Certainly must satisfy. And this. Scan functional. Is a meta GGA. That satisfies. These 17 constraints. So therefore. You can hope. That because it behaves. Like the exact functional. In many ways. In at least these 17 ways. You can hope. That it will not be too far away. From the exact functional. And indeed. It turns out. That with the scan functional. You can make predictions. That are. That are closer to. The experimental values. Than with the simpler functional. Or than with meta GGA's. That are. That do not satisfy. All these constraints. It does not mean. That for every. Specific crystal. Scan is the best functional. You can think. But on average. It works rather well. And because. It is guided. By universal truths. And not by fitting it. To the properties. Of a specific class of materials. It can give you. A rather unbiased prediction. For the property. You are interested in. Let's look at this stage. To where. In your input file. For quantum espresso. Which functional you take. That is in the. System block. In the input DFT keyword. There by writing. PBE. You choose the Purdue. Exchange correlation. Functional. Which is the most often used. Generalized gradient. Approximation. So the second rung of the ladder. If you would look. In the documentation of quantum espresso. You will see. Many different other keywords. And so this allows you to. By putting these keywords. At this place. You can do your calculation. With a different functional. But in this course. And also for the project. We basically stick to the PBE functional. It is a good compromise. Between speed. And overall accuracy. Again back to the chat. Nothing. Then comes. Correlation. What is correlation? Well we defined it. In classical systems. And in quantum systems. And we found that the definition. Is a bit different. Why can't we use. The same definition for both. That was the question. On the forum. And I take a few answers. That reveal misconceptions. I read. The first one here. The need for the different definitions. For correlation. In a classical system. And a quantum system. Arises from the fact. That in a quantum system. The many body wave function. Can be rewritten. In two different ways. I stop here. Because of the two. But for. How should in general. The wave function look like. You have an infinite number. Of possibilities for that. It's not in two different ways. It's in. An infinitely large number. Of different ways. But by convention. We take things like. The Hartree convention. Or the Hartree-Fock convention. But it could have been. Others as well. So when the product. Of every single particle wave function. Is taken. Then it's the Hartree method. And the Hartree-Fock method. Is when you use. The best Slater determinant. That's another misconception. Because the Hartree-Fock method. Gives you. The single particle wave functions. That lead to the best Slater determinant. These single particle wave functions. That give you the best Slater determinant. Are solutions. Of the Hartree-Fock method. You do not need to know them. In order to use the Hartree-Fock method. Which is what this statement. Incorrectly would suggest. In another long answer. That I will not read here. You find. A good description of. What is happening. With the Hartree and the Hartree-Fock. Ways of writing the wave function. But it doesn't tell you. Why that is needed. Why we cannot do just the same. As in classical physics. And. Also here. In this answer. A similar misconception. Is happening as in the first one. It also tells about. The need for a Slater determinant. Because of the. Antisymmetric wave function. Well. The Slater determinant. Is antisymmetric. For sure. By construction. But you don't need. A Slater determinant. You need an antisymmetric wave function. And there are many many more. Infinitely more. Antisymmetric wave functions. That are not Slater determinants. So. There is no reason. Why the correct solution. Is a Slater determinant. You only take a Slater determinant. Because then. At least it will be antisymmetric. But your correct solution. Very likely will be. An antisymmetric wave function. That is not a Slater determinant. So. The underlying reason. Why there is that difference. Between the classical and the quantum part. Is the. Indistinguishability. Of the particles. In the quantum system. That's a fundamental requirement. And I have put there. In the course. There is a link to. A course text. From elsewhere. Where they really nicely. Outline the. Even mathematical justification. Behind this. In the quantum system. It is a fundamental requirement. That if you interchange. Particles. Then. Nothing can have happened. To the

properties of the system. There is a complete. Indistinguishability. Every. Variant of the system. With only particles interchanged. Must behave. In the same way. And you can never trace back. Where the swap happened. That must be prevented. At all costs. In the quantum system. There is a. Indistinguishability. I really struggle over the word. That leads to this. Antisymmetric requirement. Of the wave function. And therefore. So if I would have to answer. This question myself. In a systematic way. How does this now all come together. I would say. Correlation as such. Is defined. In the quantum system. It's the energy difference. Between the independent. Particle solution. So the non interacting particles. And the exact solution. For the interacting particles. However. In the quantum system. Due to that. Indistinguishability. We. Want to rewrite. That correlation. In two steps. We first make. That somewhat artificial construction. With Slater determinants. The Hartree-Fock solution. And the energy. That we get there. So that part of the correlation energy. We give that a different name. That's exchange. And then the part. That is still missing. Between that Hartree-Fock solution. And the exact solution. That we call then correlation. Although. Exchange and correlation. Are correlation energies. In the classical sense. It would have been. Much easier. If we would have used different words. For that. If we would have said. The energy between the independent. Particle solution. And the exact solution. That we call correlation. In quantum and in classical physics. But for quantum systems. We will split. That correlation. In an exchange part. And in. In something. With a different name. Unfortunately. That different name. Is also correlation. And that. Makes the things confusing. Now with Hartree-Fock. And all the methods. You can build. On top of Hartree-Fock. The post Hartree-Fock methods. You can solve the Schrodinger equation. And quite accurately. With DFT. You can do that too. Via the detour. Of the Kohn-Sham equations. And we speculated a bit. Of what are the advantages. And disadvantages. Of both approaches. And where can you use them. In a large molecule. Would you want to use DFT. Or post Hartree-Fock methods. Somebody answered. I think in such a large molecule. Electron correlations. Will be important. And they are not taken into account. In Hartree-Fock. So we probably have to use DFT. Because that takes correlation. To some. Degree into account. But. You can see. How large the exchange energy is. In such molecules. So if exchange is large. Then maybe Hartree-Fock. Will be better again. But as this is a course. In DFT. The correct answer. Will probably be DFT. That's a sincere answer. At least. Where does the reasoning. Go wrong a bit. You say. Correlations are important. In a large molecule. But this has nothing to do. With the size of the molecule. The simple H₂ molecule. Also has. A lot of correlation energy. So even. For the H₂ molecule. Correlations are important. Therefore. Correlation or no correlation. Cannot be the issue here. The problem is more time. Post Hartree-Fock calculations. Are much more expensive. Than DFT. And the length. Of the calculation. The compute time it requires. Will depend on the number of atoms. In the molecule. Or the crystal. So if you want to calculate. Such a gigantic molecule. No way that you will be able. To do that with an expensive method. As post Hartree-Fock. Post Hartree-Fock will be more accurate. But. How does it help. To have a more accurate method. If you cannot. Solve its equations. So therefore. The method. That is allowed. That your computer. Do allow you to use. Is DFT. Not for accuracy reasons. But for time reasons. Then we still have to. Numerically solve. These cone charm equations. And we discussed. The general scheme for this. This is an iterative solution method. You will start. With some density. Wherever it comes from. It can be the starting density. Or it can be the density. At some point in the procedure. From the density. See the first Holmberg cone theorem. You construct. The potential. The single particle potential. That will enter in the cone charm equations. So you can write down. The cone charm equations. You solve them. To get the one particle. Functions ϕ_i . From which you can construct. The total density. The new density. Of this iteration. And then you will look. Whether that new density. Is identical. To the density. From which you started. So whether that density. Is self consistent. If you solve the cone charm equations. To get a density. Is that the same density. That you needed. To create the cone charm equations. They should be the same. Otherwise your problem. Is ill defined. So this iterative loop. If they are not identical. You will. Get a new density. With some variation. Into a new old density. And you repeat the cycle. And you keep iterating. Until they are identical. And then your problem is solved. You

have found the self consistent density. This is reflected in your input files. Because these cone charm. One particle orbitals. They will usually be expanded. In a basis set. And in the case of quantum espresso. This is a basis set of plane waves. The sky. Are plane waves. And that is an infinite summation. That is a basis set of infinite dimension. But in practice. You will limit that summation. At some point. And that. That point is determined. By the `ecut_wfc` variable. So the higher. This number. The higher terms. In this expansion. In basis functions. Also the densities. Will be represented. As a series expansion. With another truncation. That is specified by this number. And the decision. When is the old density. Identical to the new density. You will need a numerical. Criterium by this. And this is the. Threshold. If that difference. However it is calculated. If that difference is smaller. Than the number you put here. Then they will be considered. To be identical. You will not. This is another part of the input file. For quantum espresso. By the way. This new density. That you find here at the end. You will not use that one. Immediately. If you use the old density. For the next iteration. You will somehow mix it. With the old density. That you had already. In order to dampen. Some large fluctuations. In the iterative cycle. And the kind of. The number that tells you. How much of the new density. Will you use. And how much of the old density. That is determined. So several aspects. Of your input file. For quantum espresso. That reflects. This general discussion. Of the numerical. Solution methods. You can also see. In the output file. When you have reached. This self consistency. So I see here. The total energy. In the first iteration. Minus 93.4. 5. In the second iteration. Minus 93.452. The difference. Is of the order of 0.002. Rydberg. And if you continue. This for a few iterations. In the end. It will give you. Minus 93.452.555. And the difference. With the previous iteration. Will have many zeros. So then you can say. The density is identical. Now the density is self consistent. I asked you at some point. Which. DFT codes. You may have used in the past. And these are the codes. That some people have used before. Most of you did not use. Any DFT codes. It is nice to look at this list. Because they represent. Classes of methods. Depending on their basis set. So SIESTA. GAMIS and Gaussian. Are local orbital basis sets. That means functions. That are defined. For a particular position in space. Connected to an atom typically. And you will create. Your crystal density. By expanding this in. Orbitals that are located. At specific atoms. In contrast. To the all-electron methods. Where you have basis functions. LAPW basis functions. That are defined. Over the entire crystal. So they are not located. On a specific atom. The same is true. For the. Pseudopotential and plane wave codes. They are simple. Basis functions. Plane waves. That are defined. And you can computationally. Afford this. With the potential. Of your nuclei. To replace the nuclei. With a pseudopotential. Is an accuracy of fictions. So if you. Then you work with. The vast calculations. Which is what. It's rather. How do you. Use this. This element. Is given by the. SSSP library. Where you see here. The link. And you can download that. In your virtual machine. You can go to this place. Download that star file. And keep the. Pseudopotential files. For the elements. That you are interested in. So that's. The short. Best way. To have a meaningful. Pseudopotential calculation. Is to take. Trusted pseudopotentials. From libraries. Like this one. OK. Let me first. Wrap up the scientific part. And then I will go to the chat. Once more. So once somebody asked. At this stage in the course. Can you give. Anybody without. A mathematical or physical background. Can understand. And that was a nice challenge. So I thought a bit about it. And I came to this answer. I would say first. First key. Ingredient of DFT is. The density. Contains all the information. Every. Observable property. About a crystal or a molecule. Is in principle. Contained in the density. So you can do. Quantum physics with densities. You don't need wave functions. And secondly. You can find that density. By solving a hypothetical system. Of independent particles. And therefore. That is much easier to do. Which. However does not mean. That you make approximations. You will find the exact result. Provided you know. That universal exact exchange. Correlation functional. Which we don't know. And which we have to approximate. Or guess. So that's in a nutshell. The two main. Ingredients. Or the two main messages. Behind density functional theory. There is not much. To say about the. Hands on part this week. So next week. We will. In the coming week. You will look at crystallography. And you will feel. That this is a very different topic. Much more visual. Much less esoterical. As DFT itself. But also needed. If you want to deal with crystals.

In the let's play section. You will play with one or more crystal viewers. And you will consider. The importance. Of working with CIF files. And in the project. As I said in the very beginning. The teams will. Be requested to make. A first sketch of their work plan. Just as in the previous weeks. I will now. Give you five minutes. To go to a different form. Where you can. Oops. And I see that meanwhile. There is some. Message from YouTube. That the video connection. Is a bit slow. So I hope that this doesn't disturb. The ones who are watching live. In any case. You will get. Five minutes. To look at this form. To formulate there. A summary for the past week. And a suggestion. For an exam question. You may by the way. Look at the previous weeks. Where that collected information. Is available under the video. And after that. We will look at the chat. Whether there is still something there. To address. So first these five minutes. Okay. That's done. Aha. Okay. For luck. The YouTube interruption. Was not. Very long. Okay. So. Thanks for. Your contributions here. And if there is. Anything left to ask. Or comment about. The past week. Then now is the time. I don't expect. There will be. Because. Otherwise you probably. Would have put your question. But let me nevertheless. Wait for. Half a minute more. Okay. I don't see. Anything appearing. So next week. We will see each other back. And then it will be. The comments. The feedback. About crystallography. So see you next week.