

Computational Materials Physics (2024)

webinar 02 – Density Functional Theory, part 1

Today we have the feedback webinar on the first session on density functional theory. This will be the workhorse of our course. We will spend two weeks to understanding the concepts behind density functional theory. And the past week was the first one. But before going to the science, a little bit of housekeeping. And that will be very short. I just remind you, if you haven't done so already, please register yourself properly at Zulip. And configure the administrative news stream in such a way that it sends you an email when I post a message there. Because that will be the only way of communication in this course for urgent administrative messages. So in case something would go wrong. Even if I get ill. And a feedback webinar cannot take place, for instance. Then it will be announced in that way. So that was the only little bit of housekeeping information. Let's jump into density functional theory. And you had a few items there in the past week. The first one was functions and functionals. That is, by most people. Very well understood. I asked you to give some examples of functionals that you have met earlier in your education. And let's review some of the suggestions that you gave. Somebody gave this possibility. I have y equals x plus one, which is a function. And then there is written take capital F of y . And define that as y plus one. Well, that's not an example of a functional. This is still a function because y is x plus one. So if I fill out this x plus one at the right hand side, then we have F of y is x plus two. And that's still a function. So a functional is more than changing the notation. It's not by going from a lowercase f to a capital F that this magically becomes a functional. No, you need something differently. So another suggestion was somebody has met functionals in a finite element course. I googled for this because this example was not familiar to me. And I must say I didn't find anything that gave a connection between finite elements and functionals. I found a lot of pages with finite elements and functions, basis functions in a finite element treatment. But no functionals. So maybe this is just my ignorance. But it looks like this is not a proper example of a functional. If you recognize your answer and you think, no, no, I'm really sure there were functionals used in finite element treatments, then feel free to give me some more details. I would be happy to learn. Examples that are functionals. Well, the most straightforward example that you may think of, and several of you gave that example, is the integral of a function. If I define here at the bottom the area under that function f between the points a and b , so the shaded area on this picture, this is a number, and that number depends on which function I use here. If I take a different function, that will be a different area. So you have as input a function, and as output a number. Take another function, you get another number. That is the behavior of a functional. So this was a correct example. Someone else gave the norm of a function as an example, and that's an elaboration of that integral idea. You take again the integral of a function, but now the function squared, and then you take the square root out of it, and that is a definition of the L_2 norm of a function. So this norm, or any other norm, connects a function as input to a number as output, and that's indeed a functional. Someone gave an inner product on a Hilbert space as an example, and I just put here the Wikipedia page that discusses this a bit. Sorry. So I will not read that article, but you can read it for yourself later if you want so. The idea is, if you have a space of functions, with some properties, some good properties, this is then a Hilbert space, I define this now very lousily, and you can define an inner product on that space, an operation where you take as input one or two functions, and as output it gives you a number. So that's indeed what you expect from a functional. Very well known functionals that some of you have suggested, Laplace transforms, the top line here, or Fourier transforms, the bottom line. You take a function, a function of time, you plug it in in this interval, which is now an integral from zero to infinity, and you multiply the function with this exponential, the time is the argument of the function, but you integrate over time, so there will be no time anymore after this operation, and only the parameter s remains, and so the value of that integral at that parameter s , that is a number. And of course you can do that for all different values of s , and you can then have the Laplace transform as a function of s , but for a given value of s , this is a functional, and exactly the same for the Fourier transform, with this difference that you have,

this complex exponential here. An example that has been suggested by many, I put a few ones here, that's the Lagrangian, which itself is a function of generalized position, generalized speed or velocities and time, and if you now take the integral over the Lagrangian, between two time intervals, the number you get then, that's the action, and so this what is written here at the bottom, that's the action functional. It takes the Lagrangian function as input, and it produces an output that is a number. So in classical mechanics, in a more advanced discussion of classical mechanics, you will find this many many times. Somebody gave it a somewhat different name, the energy functional in calculus of variation, or a variational method, that is the Lagrangian. And also in quantum field theory, which is less my comfort zone, but someone suggested, and every year there are people who make the same observation, in quantum field theory, the Feynman propagator, the path integral derivation, that is an example of a functional. So we can be sure, functionals, we now know what mathematical object this is, and although it is not something many of us meet on a daily basis, you have met it before. So one of the three words in the name density functional theory, has been defined by now. Then we turn our attention to the Schrödinger equation. That is the equation that density functional theory will try to solve. Not in the way that we are used to, but the goal is finding a solution of the Schrödinger equation. And I asked you to list the different ingredients that appear in the Schrödinger equation, in the Hamiltonian of the Schrödinger equation. This gave somewhat opposite reactions. Some people complained, this is something we have seen already many times, in many different courses. While other people said, I am sorry, but I don't feel very comfortable with wave functions, and how the notation of wave functions is used. So we have a different background here, and yes, I take one step back to build things up from the ground. So for the people who have seen this many times, bear with us, it will not stay like that. You have to survive this stage, and then newer things will appear for sure. But we want to have everybody on board, so therefore this step back. So ingredients in the Hamiltonian in the Schrödinger equation. Well, we discussed ingredients, the Hamiltonian itself, the wave function, the energy, but this question here was specifically about the Hamiltonian, the H . And an answer that several people gave was, well, you have a Coulomb interaction between the electrons, a Coulomb interaction between electrons and nuclei, and between the nuclei. Which is correct, but which is not complete. So one reason for asking this question was to draw your attention that also the kinetic energy is an important part in the Hamiltonian. Kinetic energy of the electrons, and kinetic energy of the nuclei. So in general, the most general Schrödinger equation for a system of nuclei and electrons and remember the previous week, our quantum system consists of nuclei and electrons, so the most basic Hamiltonian for that quantum system has these five types of terms, the three you see here on the slide, and then the kinetic energy for electrons and nuclei. Several people gave that as an answer, so you have here indeed these two kinetic energies and these three interactions. But some people added also other terms to that. For instance, electron-phonon coupling and spin-spin interactions. And that is not correct. That most basic Hamiltonian has no spin-spin interaction. You have seen by now the topic on the Hartree-Fock equation, or the Hartree-Fock approach to solve the Schrödinger equation, and there you have seen how out of symmetry, out of statistics, you find this exchange term where spin plays a role. So this is not built into the Hamiltonian. You do not have in the ab initio Hamiltonian a term where two spins are interacting. No, if you take this most basic Hamiltonian with five types of terms and solve that according to the recipes of quantum physics with the proper Fermi direct statistics, then spontaneously there will be an interaction between the spins implied in the result. So spin-spin interactions, are not a part of the Schrödinger equation, are not a part of the most basic Hamiltonian. The same for electron-phonon coupling. If you do have the kinetic energy terms of the moving electrons and the moving nuclei, and you would solve the Schrödinger equation as a function of time, then everything is moving, and if there is an interaction between these two types of moving objects, then that will be part of your solution. So the electron-phonon coupling is not something we have to add to the Schrödinger equation. If we solve it correctly and completely, it will spontaneously be contained in the solution. Of course you can make simplified Hamiltonians, phenomenological Hamiltonians, where we will not try to solve the ab initio

Hamiltonian, but where we take a kind of fake Hamiltonian that has a few terms that are meant to mimic the things we can get from the full solution. And so if you say, I have seen a Hamiltonian with electron-phonon coupling and with spin-spin interaction, that will not have been an ab initio Hamiltonian, that will have been a human constructed Hamiltonian, that is meant to capture in a more simple equation the behavior of the true physical system of electrons and nuclei. After having zoomed in on the Hamiltonian, we also looked at the wave function, that is another ingredient of the Schrödinger equation, and here we asked ourselves, the wave function is a function, so something that goes from one source space to a target space that is a real or a complex number. So what type of function is that? What is the source and what is the target? And I asked you this for an example of two spinless particles, where you had to find what is the right source and target, and everybody found that this is solution C, so you have two particles, that means two spatial degrees of freedom, so six degrees of freedom in total. These six degrees of freedom, they are the variables of the wave function, and the wave function maps these six numbers onto one single complex number. So from \mathbb{R}^6 to \mathbb{C} , that is the operation that is done by the wave function. And the last ingredient of the Schrödinger equation was the total energy, where I will not say anything else, but I just repeat a comment that somebody made in the previous years about this, a comment that I like. It expresses the wonder of a physics student who suddenly realizes that this E from the Schrödinger equation, that this is an experimentally observable property, something that is not always emphasized, but yes, you can measure this, this is a physical number, and we have conceptually sketched how you measure this. So it is the energy difference between the absolute ground state of a quantum system and the state where all the individual particles, all electrons and all nuclei, are at rest and at infinite distance from one another. So if you measure all the steps that you have to do to your system to reach that state, put in energy to let the system vibrate, to let the system melt, to let the system vaporize, to let the system into a plasma, all these energies together, that is the total energy. Before we move to the Born-Oppenheimer approximation, let me look at the YouTube chat, whether there is any question there. Jack asks, is it possible to send a test email via Zulip? Yes, good idea, I will do that later today. So you will see, if you receive that email, you will see that you have correctly configured the administrative news stream. Good, next topic, the Born-Oppenheimer approximation. Here, I explained what the Born-Oppenheimer approximation is, and then I asked you, when is it not valid to make that Born-Oppenheimer approximation? Let's look at your suggestions. The reasoning that many of you follow, and it's a very logical reasoning, is, well, the Born-Oppenheimer approximation that assumes static nuclei, so therefore, when the nuclei are not static, this approximation will fail. So we have to look for situations where the nuclei are not static. What are the options? And somebody suggests, well, if you deform a metal, then the nuclei are moving. So maybe then, the Born-Oppenheimer approximation is not valid. That's a fair attempt, but it's not correct. And why not? Well, this is a good case to illustrate what we mean by a nucleus that is moving slowly. The nucleus has to move slowly with respect to the electrons. How fast do electrons move? Well, a fair fraction of the speed of light. 10 to 70% of the speed of light, depending on which type of electron. That is the speed of electrons in an atom, or in a crystal. So a nucleus that is moving at, say, 1% of the speed of light, is still rather slow with respect to the electrons. Well, if you deform a metal, how fast will your nuclei move? By far not 1% of the speed of light, much, much slower. So, deformation of a metal, that's a static case. The nuclei are at rest with respect to the electrons. Their speed is negligible. Other people think, well, if we heat the crystal, then the nuclei will vibrate. You will have these typical phonon frequencies of terahertz. So maybe the speed of these nuclei is sufficiently high to invalidate the Born-Oppenheimer approximation. Again, no. These nuclei that vibrate for thermal reasons will not vibrate close to a fair fraction of the speed of light. So also at high temperatures, the Born-Oppenheimer approximation remains valid. Let's then increase the temperature even more, and bring that crystal into a plasma, where nuclei and electrons are separated from each other, and both move with some speed. So here, depending on which type of plasma it is, here it can happen that the speed of the nuclei is so high that you cannot apply the Born-Oppenheimer approximation. So this

is a valid example of the Born-Oppenheimer approximation. Other examples, let's look at the opposite. Let's look at systems with nuclei that are so light that they are not much heavier than the electrons. And the easiest case where you can realize that is the hydrogen nucleus, which is just one proton. It's still 2000 times heavier than the electron, but it's the lightest nucleus you can have. And indeed, if you treat a system with hydrogen nuclei and electrons, it is not so obvious that you can consider the nuclei as infinitely heavy and therefore static. So an exact treatment of a system with hydrogen inside would be a treatment where both the nuclei and the electrons are treated at a quantum level. And that's not the Born-Oppenheimer approximation. The Born-Oppenheimer approximation essentially tells that we can take the nuclei as classical particles and that only on the electrons we have to impose the quantum behavior. So systems with hydrogen can be a case where the Born-Oppenheimer approximation is not valid. And another example where this can happen is if you have situations where this kinetic energy term is very important. In the Born-Oppenheimer approximation you have cancelled the kinetic energy of the nuclei, but if that term is needed either for symmetry reasons or in that example here of fibronic coupling, where the motion of the nuclei is really relevant for the property you want to describe, then also then you cannot make the Born-Oppenheimer approximation. Or another example if you have very strong external fields like a very strong laser field, also then Born-Oppenheimer is not possible and I will give a bit more details why this is right away. So let's summarize all these examples. I see three categories when Born-Oppenheimer is not applicable. And the first category is that one where the nuclei are moving so fast that the electron system has no time to settle in immediate equilibrium with the nuclear positions. When can that be? Well, in the one we just had, this ultra-short experiment, if you have a very strong laser pulse that will very rapidly move the nuclei and the electrons, then the equilibrium between nuclei and electrons is broken. And if that is a very short experiment, because the pulse is so short, it will not have the time to get in equilibrium and you have to describe that experiment without the Born-Oppenheimer approximation. This can also be in somewhat simpler situations. If you do ion implantation in solids, you shoot a beam of say, fast protons on a solid, that these protons they move very fast, much faster than the motion of nuclei in a crystal. And there is no time for immediate equilibration. So, no Born-Oppenheimer approximation. Or, if you have a chemical reaction where your molecule goes to a transition state, a specific position of the nuclei where the reaction can turn into the thing you want, it can fall back or it can turn into the product you want to create, well, often these transition states are very difficult. And when the system reaches that state, that very important state for the reaction, it can happen that there is no time for the electron system to equilibrate with the nuclear system. And you cannot use the Born-Oppenheimer approximation to describe the molecule at that state. Which means, if you want to model a complete chemical reaction, including a nuclear barrier, that this may not be possible within the Born-Oppenheimer limitation. A different category where Born-Oppenheimer fails is for these ferrilite nuclei, so the hydrogen nuclei. We discussed that. And a last category is when you have these solutions of a molecule or a crystal with a particular geometry of the nuclear positions, your electron system in equilibrium with that, and a different arrangement geometry of nuclear positions, also with the electron system in equilibrium with the transition barrier between these two states would be very small. A quantum system that is in that situation, what will it do? It will tunnel from one solution to the other one through the transition barrier. With a low barrier it can easily tunnel. So your system and therefore making the nuclei fixed and static is a bad approximation. So in that kind of situations too, Born-Oppenheimer is not working. So much about Born-Oppenheimer. For the rest of the course we will apply the Born-Oppenheimer approximation. All practical quantum chemistry calculations today are within the Born-Oppenheimer approximation. So it's universally made, it works in many many situations, but nevertheless it was good to take a few minutes to realize that it doesn't apply everywhere. No questions added. So we continue with the Hartree-Fock method and the connected related family of post-Hartree-Fock methods. Where you saw the explanation in the video, I will not repeat that, but I will add here a few more examples of post-Hartree-Fock methods in quantum chemistry courses. The reasoning behind the question goes as follows. I was surprised to see that the exact

solution was outside the Hartree-Fock solution was the best solution for a single Slater determinant. And these exact post-Hartree-Fock methods would combine these single Slater determinants. They would have a sum of excited state Slater determinants and how can that be reconciled with that picture? You have indeed the space of all single Slater determinants. And in full CI and in post-Hartree-Fock calculations in general, you are making a linear combination, you go outside the subspace of single Slater determinants. And that's how you can reach the exact solution that indeed itself is not a linear representation of the ID. Step by step we move into the ingredients for density functional theory. Another one that we had to discuss was the external potential. And it's the term that defines which system we are dealing with. It's the only place where you really see once you have made the Born-Oppenheimer approximation, so the nuclei are static, you do not care about which system you are dealing with. But once you have made that approximation then the only place where you can see which system am I dealing with that is in the external potential. You see there the position coordinates of the nuclei and you see that the external potential is equal to the nuclear charge. So the external potential fully defines which system you are dealing with. And I asked you to write down the external potential in a .gif file where you can read the full explanation because there are several ways how you can answer this question. The only goal was to make you think consciously for a while on how that external potential looks like .so I have never thought about how the electron nuclei terms uniquely define a system but once you realize that it's obvious. And then the last object of this lecture is the density of an oxygen molecule. Now we need to understand density and well we defined the density and I asked you here as a little application take the number of electrons in that molecule so sixteen. Most of you have answered sixteen some of you wrote one which is tempting because many body wave functions they are typically one but the density which is basically the modulus squared of the wave function but really in a way that it takes the number of electrons into account the density if you take this first part of density functional theory we haven't said anything about what density functional theory is we only prepared the scene we introduced all the different objects and the density functional theory I will say something about the practical part and about the project work in a few minutes I will also deal with your questions and comments if you have some so you can still put your questions in the chat and there I asked you in the next five minutes write down what is your summary about these topics what should you surely remember about this it's a good exercise for you right now also if you watch these videos later it's a good exercise to make if you do not watch live and I will then put the last week under the video of last week and you can use that information while studying and as I said before I will also take a few of the practical part and on the project work ok thanks for your contributions let's then say a few words about the practical part for this week I hope you enjoyed this video which was running your first DFT calculation and obviously without knowing yet what exactly you are doing there but that insight will grow over the weeks and I hope you will also take a look at the DFT calculation on your own laptop that is very meaningful if you come from a totally different field so yeah it's very useful anyway we will see you soon bye instructions and you may have seen that the kind of problem that was described here was also mentioned on that page and that there were several links to solution sites for that problem so well with this link added you have now yet another way how to address that situation and there was another question somebody who said yeah can it can we change the keyboard inside the virtual machine because by default it's on QWERTY and if you prefer to use a different keyboard and that can be annoying so yes that is possible and it's even addressed in the frequently asked questions of quantum mobile I have put a link to that in the link in the description below. as a reply to this question on Zulip and you see the start of the screen where you have this explanation also here on this on this slide so the in this black bar here you have the link as well so you could type this one and directly go to the explanation. There were no explicit questions about the practical aspects of quantum mobile. so I assume that this is going fine for everybody that you have the virtual box installed that you can run that first example without errors so if that is the case then you can be reassured then everything is all right and your understanding in what you do when you run such a calculation will grow in the

coming weeks. About the project so I asked you to for the forecast of quantum mobile. credit students to indicate whether you want to be assessed via a project or via an exam I have this information now from almost everybody there are two people that are still where I still have to know that I still have to contact in order to be sure that they really are in the course and want to submit this form or not. I hope this will be settled today such that from tomorrow onwards the project teams can be assigned so far ten people signed up for the project including some international volunteers so that means that we will be able to form three to four teams and the topic will be for most teams the topic that was indicated on the project site. There are two people who suggests a different topic one that they are working on themselves for other reasons so I will still email these two people to see how this can be practically organized I will come to the questions you have put in the YouTube chat after this brief outlook on next week which is very simple we will continue with the density function of quantum mobile. Now really starting with the DFT formalism that is based on the first two theorems of Hohenberg and Kohn and in the practical part you will learn something about the convergence testing for your calculations something that is a very important step at every time you start a new computational project so also when you start the project for this course. convergence testing will be the first thing you have to care about having said that let's look at the YouTube chat because there were two questions there Thomas mentions that he forgot to mark the of to to check the mark as complete button on the core site is that a problem no because for finding out whether you have submitted all tasks I look at the individual tasks at the actual content and not at the marked button but it's never bad to mark that button because then also the automatic counting of the site is up to date so please do it but it's not really a problem if you forget to do that and then William has apparently already some experience with DFT codes and next to the quantum espresso code for this course he also uses Abinit and he did twice the same system with these two different codes even using the same code. pseudopotential we will come to that in the coming week what that means pseudopotential and he finds that the total energy is different in these two calculations so how can you be sure how can you know when you can use total energies used in one code for another code well the short answer is never do that why I told you total energies are observable properties so in principle any DFT codes would give you the same total energy in reality however DFT codes make an enormous approximation for the value of that total energy they work not with all electrical codes but with total energies total energy. So the problem is that these electrons are not the electrons of the problem which is something the all electron codes do no they forget the electrons that are close to the nuclei they replace the potential of the nucleus by a pseudopotential that takes the effect of these electrons near the nucleus into account and the electrons near the nucleus they are often not at all involved in chemical binding so they are kind of not interesting so you can get away by neglecting these but that means that the total energy is not an observable quantity anymore because you have removed the enormous energy that is present in these tightly bound electrons close to the nuclei so therefore if you use a pseudo potential then the value of your total energy will be less than the value of the electrons near the nucleus. So therefore if you use a pseudopotential then the value of your total potential is less than the value of the electrons near the nucleus. energy will have no experimental meaning. If you use two different pseudo-potential DFT codes with two different pseudo-potentials, then the energies can never be compared. Now what William did was using two different DFT codes with the same pseudo-potential. Then you could hope that these values are rather close to each other, however, in both codes you use a finite basis set, and therefore, that's an approximation too. If you would use an infinite basis set in both codes, then you would probably evolve to the same number. But with a finite basis set and a finite basis set, then you would probably evolve to the same number. But with a finite Kmesh, topics we will discuss in the coming week, there will be differences in your total energy. Unless you are in really high precision calculations, and you know very well what you are doing, so unless you are in that situation, I would never use an energy calculated in one code as input, or as a comparison for another code. Energy differences, that's another matter. That can be done. If you have two geometries of the same crystal, and you calculate the energy difference between these two geometries with one

code, and with another code, then these numbers will very likely be much closer to each other. But not the absolute value of the total energy itself. And William asks a follow-up question. Would it in principle be the same? Are you calculating formation energies or cohesive energies? Aha, well that's exactly what I just said. For a formation energy or cohesive energy, there you subtract two energies, so that's an energy difference, and that is comparable across codes. At least as long as you use the same exchange correlation functional, another ingredient that we will discuss in the coming week. Okay, so much for the questions, unless there would be another question popping up right now. I don't see any. So we start with the question. Stop here, and I'll see you in one week from now, and we will continue the DFT discussion. Bye bye.