webinar 03 – Density Functional Theory (part 2)

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This is the second feedback webinar on density functional theory. Last week, or for the study part, two weeks ago, you collected a lot of ingredients, and in the past week you have prepared a meal with these ingredients. Now it was really about density functional theory itself. But before coming to the science, a little bit of housekeeping. So for the projects, we have a rather large number of project teams this year, eight different teams. You should have received a mail yesterday with the contact info of the other people that are in your team. And here I just remind you, what is the work plan. So one week from now, there is a due date for a short work plan for the project. So a short description of how you plan the work of your team, how you will get to your goal. On November 11, there is a milestone with a short status report and actual calculation results. The results on the convergence tests and what are convergence tests you already met in the practical work of the past week. And then the actual project deliverables, the paper and short video, these are due on December 7th. These dates are mentioned in the overview with due dates that you have in the practical info on the website. but here just as a reminder and just in case people from the chemistry department of Ghent university if they would see this video then be assured that for the chemistry students there is a different timeline with a somewhat different project so they should not get confused by these dates another administrative issue and maybe just check whether on Zulip whether you can see the messages that are posted I see several messages a week are posted good questions and often with answers provided by yourself so that's very good and if you have configured the site as described then you should also get an email copy of the messages that I post in the administrative news channel and as a check you can see did you receive an email last Tuesday when I announced that the recording of the previous week was available I've put that in the administrative news channel and you should have received an email copy of that. so if that is okay then you can be assured that everything is all right at your site oops now I remind I'm reminded that I forgot to insert something these are old data I will repeat that next week sorry good then we are ready to go to the scientific part so with all the ingredients that you collected two weeks ago let's construct density functional theory and the first step in this is the first theorem of Hohenberg and Kohn where you felt well quite confident that you could explain what is that theorem and what is its meaning and the visual reminder about this is a bijective connection a one-to-one connection between the set of external potentials which means all molecules and crystals that can be made in the universe and the set of all ground state densities that correspond to each of these molecules or crystals so there is such a one-to-one connection possible and what does that mean well it means that we can go from one statement that we knew to a new statement and the statement we knew was this one that every observable property of a system can be expressed as an expectation value of a wave of an operator in the wave function so if you make a bracket of the wave function and you you put the operator inside then the result of that operation is a property of the system so this is something we knew in wave function quantum physics in technical language we would say every property is a functional of the wave function but this first theorem of hohenberg and kohn this one-to-one connection between external potentials and densities means that every property can also be expressed as a functional of the density you don't need to know the wave function if you know the density that is sufficient that's the first theorem of hohenberg and kohn and i asked you go to the page on density functional theory in wikipedia read what is written there compare it with what has been told in the corresponding video and discuss similarities and possible differences so let's have a look at what you have answered somebody writes the wikipedia explanation is less intuitive but more robust whatever that means and includes for instance a definition of the universal functional now i'm not sure whether i agree with that statement because if you look to the wikipedia page what you see here at the bottom of the of the screen is a screenshot from that wikipedia page where indeed the hohenberg-kohn functional is defined as the sum of a kinetic energy functional and a particle-particle interaction functional and it is told that this is a universal functional of the density it does not depend on the external potential so it does not depend on the actual crystal or molecule that you are discussing you can formulate that functional once and for all so in that sense that hohenberg-kohn functional is defined but it is a definition that is just a formal one not a practical one it tells that there is this functional but it doesn't tell how that functional looks like there is no recipe you cannot write it down and we will see that this will carry over to the exchange correlation functional that is on similar footing with the hohenberg-kohn functional and it is that is the the constructed later on in this module but also that exchange correlation functional in principle we know what it is we can perfectly define what it is but there is no recipe you cannot write it down so you cannot evaluate it you cannot determine its value in a particular situation so i would be careful with the statement that the hohenberg-kohn functional is defined at the wikipedia page defined only in the formal sense someone else commented that he or she found other sources where this theorem is derived not with intuitive reasoning but with more mathematical reasoning and this person found the mathematical reasoning on the reasoning more satisfying and fair enough that depends on your mind some people have a mind that likes conceptual descriptions other people have a mind that likes mathematical descriptions but for those that prefer mathematical descriptions this statement reminds me to due to that statement i want to remind you that on the page of the course with the first Hohenberg-Kohn theorem at the bottom there is this optional video with a mathematical derivation of the first theorem so a proof a mathematical proof of the first theorem which is the original proof that Hohenberg and Kohn have given in 1960 something and quite surprisingly for a broad class of quantum systems that proof fits on one page so it's a quite straightforward reasoning it becomes more complicated if you want to generalize it to all quantum systems but for a particular subset it is straightforward to do and that is probably the proof that you may have found in the first Hohenberg-Kohn theorem. in other sources as well there were several people that pointed to something that was an extra on the wikipedia page something that was not discussed in the video namely that two external potentials that correspond to the same density that they need not to be really identical they are allowed to differ by a constant and that constant is not relevant for property predictions if you go through the formalism to predict a property for a quantum system well in that procedure the constant will disappear it has a lot of similarities to making a derivative and adding a constant to a function if you then make a derivative well that constant disappears here it will be a functional derivative but the idea is the same another analogy, and that is what is drawn there at the right hand side, it is quite analogous to the situation in classical mechanics where you wonder what is the potential energy of an object in the gravitational field of the instruments? the earth. If you put that object on the second floor of a building and you express that potential energy with respect to the floor of that level of the building, or you express that energy with respect to the ground at the front door of the building, so you have chosen a different point of reference, you have added a different constant to the potential energy, but for all observable properties, like the acceleration that that object will feel, the time it will need to fall over a distance of one meter, for all of these observable properties, the value of that constant does not matter. So something very similar is going on with two external potential elements. that differ by a constant. So what is then a good summary? One of the examples where you gave a quite complete answer to the comparison between the Wikipedia page and the video. One of the similarities is that the final conclusion is, of course, the external potential is in a unique way connected to the ground state density, because that is the essence of that theorem. In the video this was explained with surjective and injective functions, and the implications are discussed. We can do quantum mechanics without the wave function, just with the density, whereas in the Wikipedia page they do this in a more mathematical way, and they also introduce that Hohenberg-Kohn functional, which we postpone until the situation where we have the exchange correlation functional, and they also stress that the spectrum of the Hamiltonian is also a unique functional of the ground state density. And that statement is something where I want to elaborate upon right here, because that is a question that is almost every year asked. And I repeat here the way in which it was asked last year, and somebody said the first Hohenberg-Kohn theorem specifically refers to the ground state. Does this mean that the information about excited states are not captured by the density, that we still need the wave function for the excited states, or is that excited state information still available in the density? There is a straightforward argument to give the answer here, and let me first write in somewhat different ways the visual image from the video, where we had the density. I start here in the reasoning with the density, that's one to one connected to the external potential, that is what the first theorem tells. Once you know the external potential, you can write the Hamiltonian of the system, because the external potential is just one of the terms, one of the set of terms of the Hamiltonian. With the Hamiltonian, you can write the Schrödinger equation, and in principle, if you have an exact solver, somewhere available, you can find the ground state wave function of that system by solving that, by solving the Schrödinger equation with this Hamiltonian. No surprise there, we go from the density to the ground state wave function. However, once you know the Hamiltonian, you can also search excited state solutions of the Hamiltonian. You can also search excited state solutions of the Hamiltonian, and you can find the wave function and the corresponding energy of the first excited state of the system, and also the second excited state, and so on. And that means, you see this happening here on your screen, that means that that ground state density from which we started, implicitly still contains the information for all the excited states. We can go from the density to all the excited states. So yes, the ground state density, and I stress the ground state density, the ground state density contains all the information about the system, be it in the ground state or in any excited state. So that first theorem is really a very powerful statement. The second part of that question was, well, if the density is really just as good as the wave function, and we just confirmed that it is, what is then the reason why we never learned to do quantum physics with densities? Why do we still start learning it with wave functions? And the answer to that is in what was there at the bottom of that slide, the way how you find values for observable properties. If you have whatever observable property, and you want to predict that property for a given quantum system, with wave functions we know how to do that. There is an operator known for many properties, and you can make the expectation. So for example, if you have a function where you plug in the density and it returns the value for that operator, we could do that with densities. We would need a functional where you plug in the density and it returns the value for that property. But unlike for the operators, these functionals are not known. There is no recipe how we can write down these functionals. Whereas for operators with wave functions, they can often be derived from classical physics. So that is the roadblock. Therefore, you do most of your quantum physics, certainly when it is about simple systems, you do them with wave functions, because there you know the operators. I've added a few others. Some of them are from previous years, where people express how they are a bit shocked by this first Holmbergh cone theorem. And it is indeed an incredible theorem in some sense. And a question that also often returns is, if you look at that proof, the one that that was optional, that was in that optional video there it was explicitly stated and the proof makes use of the fact that this is done for a non-degenerate ground state now it's obvious then to ask what happens if the ground state of the quantum system is degenerate can you then still is that theorem then still valid and the answer is yes the theorem will still be valid but proving this is quite a bit less straightforward than for the case of the non-degenerate ground state if you search online you will find proofs for that so if you are interested you can surely look at it so much for the first theorem of Hohenberg and Cohn then comes of course the second one the second theorem that states that there exists a well the second theorem gives you a way how you can find that ground state density at least in principle if you minimize the total energy functional the ground state density will be the norm of the ground state density that is as follows let us look at the second theorem one that gives you the lowest possible total energy so the minimum of that total energy functional and as a task i had provided you with this statement if somebody tells you yeah that second theorem isn't that just a natural consequence of the first one do you really need an independent theorem for this well do you agree with that doubt or do you not agree and what did you answer there were some people who said well it's at least very logical to expect that this will happen so in that sense that second theorem is maybe not really needed it's just obvious that it should be that way if you have a density that is one of an excited states then that will have a higher energy someone else said yes i agree with that statement i shared that doubt because after all we have the variational principle that tells us that the wave function is the object that minimizes the total energy and therefore if you have a density that corresponds cripples your density which is the value at each time in certain states then a be sure and do some learning in order to solve the problem it should be a wash just unless and when you have fixed measures yet on slight bombs and so on so initially the thing is you need to keep your state to that wave function, it will minimize the energy as well now, these two statements these two people that agree with that statement, they are wrong the statement is really the statement is wrong, you do need the second theorem it does tell you something that is not at all contained in the first theorem, so the correct answer is that we cannot agree with that statement and why not? well, you find it logical, you find it natural, you say it's the variational principle, but you have never proven the variational principle for densities so far, whenever you worked with the variational principle, it was with wave functions, so for the wave function construction, the variational principle is valid with densities, it could be valid, or it could not be valid, and what the second theorem tells you, including the proof of the second theorem, that is that the variational principle is valid for densities as well so you'll have to prove that independently, it's not something you can just copy from the wave function formalism because this is a subtle point, I have collected several answers, of this and previous years that describe this in a correct way so I will just flash them here, and you can read them more carefully later on if this is a point where you still have doubts so this is a long correct answer. Here are some other long correct answers and a few shorter formulations as well. So different ways to tell that that second theorem is really an independent theorem. And this is the illustration from the video that tried to make that same point. The first theorem tells you that there is a total energy functional of the ground state density that gives you the total energy. There is some object here described as this red line, a total energy functional if you plug in the ground state density on the so-called x-axis, then on the y-axis. would read the total energy but the first theorem tells that this is possible but it doesn't tell you how that red line how that total energy functional looks like it could be that this functional looks like this and if you plug in the ground state density you read on the y-axis the total energy that would be perfectly in agreement with the first theorem the first theorem doesn't tell anything more than this the second theorem tells you that the situation at the right hand side is not what happens in nature the total energy functional looks like it is shown here at the left hand side the ground state density minimizes that total energy functional so it's really a problem that we can solve. It's really new independent information that is added on top of the first theorem. Meanwhile I look to the chat every now and then so if you have specific questions don't hesitate to put them in the chat. Meanwhile we move on with the Kon-Sham equations so now it becomes a bit more practical. We have constructed density-functional theory formally with the first and the second Hohenberg-Kohn theorem. Now, with the Kon-Sham equations, we turn it into something that you can compute. You can look at the Kon-Sham equations as a reformulation of density-functional theory in single-particle equations. Single-particle equations that are much easier to solve than the original many-body Schrödinger equation. Rather than searching for orbitals of electrons, you will search for orbitals of some quasiparticles. But the Kon-Sham construction guarantees you that the density that corresponds to orbitals, all these quasiparticle orbitals, that this density will be the same as the electron density in the original system. At least, if you can make the right choice for the exchange-correlation functional. We will come to that. In order to understand better, to visualize better what the Kon-Sham procedure is, I ask you to think about the following. If you would have to devise the Kon-Sham procedure for the solar system, for the planets that are orbiting the Sun, how would the Kon-Sham method look like for the solar system? I show a few of your answers. Somebody writes, the stars or the Sun, they play the role of the nuclei. The planets, they play the role of the quasiparticles, of the electrons. These planets, they have kinetic energy, and rather than the Coulomb interaction between nuclei and electrons, we have the gravitational interaction between the Sun and these planets. There is nothing wrong there, but it's not yet a complete description of all the ingredients for the Kon-Sham procedure. This description is a bit more complete. You transform that many-body problem of multiple planets interacting with the Sun and with themselves, you transform it in a set of single-planet equations, where every planet has its own kinetic energy, where you have something that corresponds to the hard return, the gravitational energy of that planet, in the averaged potential of all the other planets, then the gravitational energy of that planet in the potential of the Sun, and then an exchange-correlation potential that is added to this. But that was what I was actually doing. I was actually asking for, so not that you have to add that exchange-correlation energy or potential, but what does it mean in the context of gravitation? Why do we need it? We will come to the precise reason why we need it. I first draw your attention to something several people have mentioned, differences between quantum systems and classical systems, and something that has been mentioned several times, that is that you have this aspect of indistinguishability in a quantum system, and how that relates to exchange and correlation. So, exchange-correlation is in that sense a typical quantum phenomenon, because it is related to that indistinguishability. That's kind of true, but not completely. I would say that correlation, as such, is a concept that you have in classical physics as well as in quantum physics. But the indistinguishability in quantum systems adds another aspect to correlation, and that is what we call exchange. So you could call the exchange a quantum feature, but not the correlation. So you can still discuss an exchange-correlation, or at least a correlation-functional, in a gravitational form of density-functional theory for the solar system. You can still discuss that. It is meaningful. It's not because the solar system is a classical system that this extra term would disappear there. So what is the reason for that exchange-correlation term in the solar system? After all the approximations you do by making single-particle problems out of that many-particle problem, you will have neglected some effects. And everything that you have neglected, that is added back in by that exchange-correlation term. That's the term that guarantees that you have exactly the same solution from the single-particle equations as from the original many-body equation. And of course, because all complexity has to come back in that single term, it's asking a lot from a single term. You need to take many things into account. You can imagine that it will not be straightforward to write down an expression for that single term. Instead, we will make an approximation of that correction term. And because it is constructed to be small, all the big effects are in the other terms of the single-particle equation. So because it is constructed to be small, also our approximation to it will be rather good. You will not make a big mistake. Let me rephrase that very systematically in the way how it was done in the video. You have your original expression above the red line. That was the Schrödinger equation for a many-body system. So if you would do that gravitationally, you would have the kinetic energy of the planets, the gravitational energy of the planets interacting with the Sun, and the third class, the gravitational energy of every planet interacting with every other planet. That is the original problem you have to solve. The Kon-Shan procedure translates that interacting system of a Sun with multiple planets into a sum of non-interacting problems. We will have one planet interacting with the Sun. That will be a quasi-planet. We will have another quasi-planet interacting with the Sun. But the quasi-planets themselves, they do not interact with each other. And what is the equation of motion that describes that quasi-planet? Well, we have the kinetic energy of the quasi-planets. We have the term that is equivalent to the Hartree contribution, the averaged gravitational interaction between the planets and all other planets. So you can imagine to time average the orbits of all planets over the solar system. And now the planet that I am considering will interact with these smeared out orbits of all the other planets. And then of course my quasi-planet interacts with the Sun. And if you would stop here, then you have just an approximation of your original problem. You have translated it in something that is one particle, yes, that is computable, yes, but that quasi-particle will not have exactly the same motion as the original planet. How do you guarantee that you solve the original problem? Well, you add that exchange-correlation term that here will be just a correlation term. Everything that you have neglected so far, whatever it is, is added back in via this complicated term. So that is the meaning of the exchange-correlation term in the

Kon-Sham procedure. There is no recipe for how it looks like. It is something that can be written down at least the functional that corresponds to the exchange-correlation potential is a functional that can be written down once and for all, but there is no recipe how we can find it. We know what it means. It is adding back in all complexity that we have removed by writing that single particle Hamiltonian, but we have no recipe to write down how that term should look like. So, that were the Kon-Sham equations with that exchange-correlation functional as the important part in it. And here, zooming in on the exchange-correlation functional, there was this article or video about something called Jacob's ladder, that is about the classification of exchange-correlation functionals. And as a quick reminder, these were the different rungs of the ladder. You start with a local density approximation that contains only the density as ingredient. You have the generalized gradient approximation where the gradient of the density is important. The meta-GGA's where also the kinetic energy density is important, and so on. Ever more complex levels of sophistication, more accurate, but in calculations more time-consuming. Why is that not so straightforward to go to higher rungs on the ladder? Okay, it takes more time, but why is it maybe for simple systems not possible to go very high on the ladder? Well, we have no recipe. Every rung on the ladder is a bit of trial and error, because the reason why even the lowest rungs on the ladder are rather meaningful, although they are still severe approximations, so the reason why we can't get away with severe approximations as LDA or GGA, is that there is some error cancellation playing in the background. In the exchange term of LDA, you make big deviations from reality, but in the correlation contribution to LDA, you make similarly large deviations from reality with the other sign. And the sum of them is more or less right. And as long as you can keep that error cancellation more or less okay, then adding more sophistication will bring you closer to the correct prediction. But because you don't know how that error cancellation really happens, you don't know which error you are making, it's trial and error, literally, and therefore it's a slow process to construct new rungs on that ladder. A few years ago, somebody made the very concise and clear statement, what's about that Jacobs ladder? Is it really that special? Okay, I read this, and yeah, so what? And I get the feeling, and I think the heart of that feeling is that Jacobs ladder is often felt as a strategy. Once you see it, well, you can get higher and higher and closer to the divine functional that will solve everything. Yes, but Jacobs ladder is not a strategy. It's a description of things that people have tried and have found to work, to some extent. But it doesn't give you a recipe how you can get one rung higher on the ladder. Once you have the image of a ladder, it's very natural and intuitive to think, this is my recipe to climb higher. But no, it's not a recipe. It's not a strategy. It's just a description, and every new rung is a next round of hard work. And an example of a family of functionals that has been developed in the past decade and that are performing quite well are the family of the scan functionals, strongly constrained and appropriately normed scan. So, in the first paper is now 10 years old, and this is an example of a family of scan functionals strongly constrained and appropriately normed scan. This is an example of a functional quite high on the ladder that is not too compute intensive and that is used nowadays a lot in practice. Talking about practice, if you then do a DFT calculation with Quantum Espresso, where do you tell which exchange correlation functional you are using? In the input file, in the systems block, there is the keyword input DFT, and there, if you put there PBE, that is the Purdue-Burke-Ernsterhof functional, a very popular GGA functional. So that is where your physical approximation is made. There you determine how close you can get to the experimental value. If you use a functional that is tested to behave well, to make correct predictions for several classes of crystals and several properties, there you tell that I make the same choice, I take that functional too, and I trust that this functional will not be too far from reality for my crystal and my property. The C in exchange correlation is correlation, so let's talk a bit more about correlation, which is the classical part, or well, which is something that you have in classical physics as well as in quantum physics, and the purpose of that module was let's try to understand what is different between correlation in the classical sense and in the quantum sense. And that's exactly the question I asked you. Why do we need a different definition of correlation in classical systems and quantum systems? And here are a few of your answers, and some people refer to special features of quantum systems that do not appear in classical systems. Antisymmetry for a quantum system, the fact that you have exchange, very closely related to antisymmetry, the fact that you have entanglement, indistinguishability, there are definitely differences between classical systems and quantum systems. Therefore, I think we can make a case that the value of the thing we call correlation, the number we put on this, if we evaluate correlation for a classical system and for a quantum system, the value of the correlation will be something different. But I would argue that in spite of these differences between classical and quantum systems, the meaning of correlation, correlation as a concept, that that is not different. So what would be my summary? Correlation is something we define as the difference between an easy independent particle solution and the exact solution. The energy difference between these two extremes, that's the correlation energy. But due to these special features of a quantum system, this indistinguishability for instance, or the antisymmetry, therefore we can write part of the correlation of a quantum system in an easy way. We have a procedure to write part of that correlation energy. And that part of the correlation energy we call exchange. What is left, that is the correlation that is not exchange. But together, that exchange part and the remaining part, that is still the energy difference between the independent particle solution and the exact solution. So together, they are still exchange in the classical sense. So the concept of correlation I would say is the same in the quantum world and the classical world. It's that difference between independent particle solution and exact solution. But in the quantum world, part of that correlation is called exchange and is defined by special features of the quantum system. . Good. Then, density functional theory with the Koncham equations is a practical, computable procedure. But we have also, mainly in chemistry, and quantum chemistry, the Hartree-Fock procedure and its variants or its elaborations, the post Hartree-Fock methods by which we can even come to exact solutions if you have an infinite amount of computing time with post Hartree-Fock you can come to the exact solution of the Schrodinger equation with density functional theory you can even with an infinite amount of computing time you can never be closer to the exact solution than your chosen exchange correlation functional would allow so this was one of the important differences between these two families of methods and I asked you in order to think about this if I take a very complicated molecule like this one here would you apply DFT or would you apply post Hartree-Fock to it well what did you answer somebody wrote given the fact that the Schrodinger equation was simple but you have to consider that if you look at the that this is a large molecule, the computational cost will be large, and that means that Hartree-Fock or post-Hartree-Fock will probably not be very useful. Moreover, correlation is not included in Hartree-Fock, and surely we will have a lot of correlation if we have so many atoms in this molecule. And that shows a misconception that is often present, that the more atoms you have, the more electrons you have, the more important correlation becomes. That's not necessarily true. Correlation is present as soon as you have more than one electron. If you take the hydrogen molecule, you can quite easily prove that correlation effects in the hydrogen molecule are very important. If you solve the hydrogen molecule with Hartree-Fock and you compare it with the exact numerical solution, you will see sizable differences that are due to the correlation between these two electrons. So correlation is not necessarily related to a large number of electrons. This here is an answer that describes the situation quite well. It's a large molecule. Lots of computation time required. That points to DFT, because DFT is the cheaper method of the two families. If you would want to use post-Hartree-Fock, you would very soon hit your computation limit, you would hit the level where the resources, the computational resources that you can use are not sufficient anymore. And if you say well, then I drop the posts in post-hard refog, I do it with plain hard refog, then you miss all the correlation effects, and you have only the exchange present. So also there you would make a prediction that is probably far away from the true result that you would measure in an experiment. So, big molecule, large computational resources required, take DFT. A few more words on these numerical solution methods. Very often these methods involve a self-consistency loop. So you start with a guess for the density, you go through different steps, and at the end of the process you find a new prediction for the density, you look to what extent that new density differs from the density you have started from, and if it is different, then you go through the loop again, and you keep iterating until the density is different. And the density that comes out of the loop, is the same as the density that went into the loop and that was used to construct part of the Hamiltonian, for which you have to solve the Schrodinger equation. So you need this iterative procedure, because you need the density in order to construct the Hamiltonian, and you need the Hamiltonian in order to find the wave functions, and there, as I said, for the density so the density is both the prerequisites and the results so that is why an iterative approach is required and that procedure has several terms that play their role in the inputs for the quantum espresso calculation so these single particle orbitals that you are searching in that iterative loop these are expressed in a basis they are functions from a function space with an infinite number of dimensions so you can express them as an infinite sum over basis functions and because we deal with computers that cannot store an infinite number of objects we have to truncate that summation and the where we truncate it that determines our numerical approximation if we truncate it after only a few terms or after many terms that will determine how close we can get to our numerically precise answer and that is the ECUT WFC keyword in the inputs it determines where you interrupt that infinite summation to express a single particle orbital. The higher, the more precise, but also the longer your calculation will take. The e cut rho that is a similar quantity, but now for a basis expansion of the density, not of the wave function. And there are other keywords, the convergence threshold that you find in the electrons block, that is the deviation that you allow between the old and the new density. Whereas that mixing beta, that is a number that determines when you have found the new density, you will not directly feed that new density inside the loop again. Because that would lead to numerical instabilities. You need to dampen the changes in the density a bit, and you will make a new density that is a mixture of the one that went in here, and the one that comes out here. This previous old one and the current new one they are mixed to form the new density that will be used here as input. And that mixing beta is a number that determines how that mixing happens. The closer that number is to one, the more there is the new density dominating. It's not a number you often have to change, but it's good to be aware of what it means. In the output file, you can also see the number of the new density. You can also see how this iterative procedure is going on. So this is at the very start. You have a total energy of minus 93.45 for some crystal in the first iteration. And in the second iteration, it's minus 93.452. So there is an 002 Rydberg difference between them. So the SCF accuracy, how close are you to convergence, is non-zero in second or third digits. It depends on estimated SCF accuracy, 002. So this is the number that determines how far away from convergence we are. We need to bring this number back to zero, as close as possible to zero. And indeed, if we look a few iterations down, here is the fifth iteration, then you see that this number has already many more zeros. So that's iterative procedure at work. I also asked you whether you were using which the DFT codes you had used before. And the blue bars, people who have never used these, and the blue bars, people who have never used these, and the blue bars, people who have never used these, used DFT codes before, these are always quite high but there are some people who have used some of the codes that are listed here, and I take this as an opportunity for some classification so we have codes where the single particle orbitals are expressed in a basis of local orbitals or we have codes, so called all-electron codes, where we have the single particle orbitals expressed in an LAPW basis, and we do this for all orbitals in the problem whether they are core or valence electrons and then we have the methods, that is also the family to which quantum espresso belongs where we neglect the core electrons and replace the effect of the core electrons by a so-called pseudopotential whereas the valence electrons orbitals, they are expressed in a plane wave basis so this is a very popular family of methods, plane waves with pseudopotentials and the method you will use in this course, quantum espresso is part of that family there is an optional set of videos in this module, you may have a look at it in the description of this video in this module, you may have a look at it in the description of this video in this module, you may have a look at it in the description of this video where a lot more is said about the different basis set methods that are mentioned here but that's an optional part only if you are specifically interested in this we use pseudopotentials with plane waves and that pseudopotential, that is something that humans have to construct somebody needs to tell you that for the silicon atom this is a pseudopotential that will represent well the behavior of the core electrons inside that silicon atom now how do you know whether that is a good pseudopotential or not? there are libraries of tested pseudopotentials available for this and I show you here one example of a recommended library where for quantum espresso you find pseudopotentials for every element of the periodic table and people have tested these to be precise so, conclusion of the scientific part for this week I make a conclusion that is based on a question that somebody asked a few years ago can you tell me what DFT is? in a way that I can explain it to a teenager so no mathematics, just concepts and make it short. So I had to think about it for a while but this is the answer I then gave and that summarizes the past two weeks, that summarizes DFT. The first statement is all information you need about the crystal or the molecule is in the density and therefore you can do quantum physics with densities you don't need wave functions. That's one part and the second statement, you can find that density by solving a system of hypothetical independent particles but you can do that only if you know that universal exact exchange correlation. In reality you do not know it, so you have to make a guess to approximate it and that will limit the accuracy of your predictions. That's it for now let me first tell what we will do next week before we come to the usual summarizing parts of these webinars. So we have now digested the mysteries of DFT now we can be for the coming week a bit more practical and visual we will look at practical crystallography and we will apply crystallography in the form of computer programs that can visualize crystals and you will get familiar a bit with how uh Vesta and other crystal viewers visualize the unit cells that you will use to do calculations on in the coming weeks and for the project there is the first milestone within a week so a draft of your work plan so now as usual I will ask you in the next five minutes write a summary of the work plan. So now as usual I will ask you in the next five minutes write a summary of the work plan. the past week in a few lines what would be the things that you feel this should certainly be remembered and formulate an example of an exam question about the content of the past week so five minutes and after that I will see whether there are questions in the chat and we can discuss these further okay let me look at the chat I don't see a question so that means everything is clear and yeah then you're ready to tackle the next week and yeah then you're ready to tackle the next week on crystallography so see you again next week same place same time bye bye