webinar 02 – Density Functional Theory (part 1)

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This is the first of two feedback webinars on density functional theory. Part 1 you studied in the past week, part 2 will be the topic of the coming week. You may have noticed that in this past week you did not actually touch density functional theory yet. We were preparing the floor. Several concepts that are needed to build density functional theory have been introduced this week. So if you think, I still do not get what DFT is about, that's normal, it will come in the days ahead. So let's look at these different ingredients that were built during DFT. The first one was functions and functionals. The word functional is in DFT, density functional theory. So we better understand what functionals are. And as you can see from the confidence distribution, that is for most people quite clear. I asked you to find some examples of functionals that you met earlier in your education. And let's go through what you have suggested with some comments. One example is somebody says the velocity of a particle is a function and the rate of change of that velocity, the acceleration, is a functional. That is not right. And why not? Let's write the expressions. The velocity of a particle at a given position r can also be written as the velocity of the particle at a position r that is reached at a time t. That's a function of either space or time. So a function. That part of the answer is correct. If you take the time derivative of that function, the derivative of a function is again a function. So if you take the derivative of the velocity function, you get the acceleration function, which is itself a function of space or time. So it's a function. Acceleration is a function, not a functional. What do we need for a functional? We need something that has a function. Something that has as argument a function. Not as argument a number, but as argument a function. So here we have one example of a functional that one of you has written in the forum. The area under a curve. If you take a function f , and you integrate it from a to b, so you have the area under the curve between a and b, that value that could be considered as the output of a functional for the area. If you plug in the function f as argument into that functional, you get as a number the area between a and b. Put another function there, you will have a different number. And the person who suggested this example related that to chemistry, where you can have a detector signal where the area under that detector signal as a function of time is proportional to the amount of substance that has been measured. So this is a practical example of how a functional can play a role in chemistry. Two other examples. The value of a function at a given point, say at x equals a, the value of any function f at that point, that's the output of my functional. Do I take another function, but I evaluate it at the same point, I may get another number. So for every other function, you get another number. That's how you have a functional from function space to number space. A related example is the norm of a function. That's a functional. So I have here at the bottom of the screen the definition of, one possible definition of a norm. If I put there another function f, I will get another number. So you can consider this expression as a functional with the function f as argument. For every new function f, another number appears. You can build on this and discover many different examples of functionals in well-known physics. I've listed here a few that you suggested. The charge, for instance, is the charge of some charge distribution. That is an example of a functional. You can define a charge density function that gives the amount of charge per unit of volume at a given position r, and then integrate that charge density function over the entire space, and the result of that integration is a number, the total charge of the object. If you put there another charge density distribution, you will get another value of the total charge. So that's a physical realization of that example of integrating over a function. You can do this with other properties. You can integrate over an electric field in order to get the energy that is contained in that electric field, and so on. Many, many functionals in physics. Laplace and Fourier transforms, these have been suggested too as examples of functionals, and that's right, as long as you consider them for one argument. Look at the bottom expression, which is the expression of the Fourier component of a function f at the frequency omega. If you stick to that frequency omega, then this is certain, this is something where a function f, a general function f, is transformed into a number. If you take this as a function of omega, then it's something different, and it is not strictly a simple functional anymore. Many, many people suggested the action functional as an example, from Lagrangian mechanics. Not surprising, it's probably, as some even wrote, the most famous functional in physics. Another example that was quoted is the total energy in quantum physics. You have the expression there, at the top left, of the total energy of a wave function, psi, in a Hamiltonian age, and you can consider that expression as a recipe for a functional. You put in another wave function, psi, and you get out another number for the total energy. And you can generalize that. Any observable in quantum physics that is associated with an operator can be considered as a functional. You have in general a recipe where you put the wave function in, and you get the value of that observable as an output. And we can keep going on. I put here some other examples from different areas of physics that have been suggested. You may read it if you want, but I hope that the point has come across, that you see what a functional is, function in, number out. That's the short summary. After this, we move to the Schrödinger equation, and we will deconstruct the Schrödinger equation, or well, you have deconstructed the Schrödinger equation, and looked at its different ingredients. This was a topic that triggers opposite reactions. Some people found this not very exciting, because they had seen this already multiple times. And other people comment, well, this was something I have not much experienced about. So this was new, I get used to notation, and so on. So, well, it's one of the things we need to try getting everybody at the same page. We focused on the Hamiltonian, on the wave function, and on the energy, and started with the Hamiltonian. And here I asked, what are the different energy contributions in that Hamiltonian? Some people said, well, you have electron-electron interaction, electron-nucleus interaction, and nucleus-nucleus interaction. Or, as somebody wrote it, in a more descriptive way, you have attraction and repulsion between the different particles in the problem. That's true, these are valid energy contributions, but they are not the only ones. There is also the kinetic energy of the electrons and the nucleus. And so you can either list them, so these three repulsions or attractions, and then two kinetic energies for electrons and nuclei, or in this more verbal description, there are interactions from repulsion between nuclei and nuclei, electrons and electrons, attraction between electrons and nuclei, and additionally interaction due to the motion of these two types of particles, so due to their kinetic energy. These are the five contributions to the Hamiltonian. The only ones, there are no other. Nevertheless, some people tried to put extra terms in there, for instance, electron-phonon coupling or spin-spin interactions. And no, these are not part of the Ebenecio-Hamiltonian. These can be part of some other heuristic Hamiltonians, phenomenological Hamiltonians that people write down in order to isolate a particular aspect of the interactions in a quantum system. But in the Ebenecio-Hamiltonian, the one that starts from the very fundamental particles and their interactions, these terms, they do not appear there. Does that mean that you do not have a spin-spin interaction, say an exchange interaction? Not in the Ebenecio-Hamiltonian. You can, however, if you analyze this Ebenecio-Hamiltonian, for instance, in the Hartree-Fock equations, which is a way to make a computable form of the Ebenecio-Hamiltonian, then you will see that in that Hamiltonian, that results from that from that approximative procedure, that there there is a term that describes the exchange interaction, that is a spin-spin interaction. But that is the result of an analysis that is a different name for a property that implicitly is contained already in the Ebenecio-Hamiltonian. But there it does not appear as an explicit term. In the same way, electron-phonon coupling, well, then you need to take the nuclei as part of the problem, but electron-phonon coupling is fully contained in the Ebenecio-Hamiltonian, if you want, but you do not recognize it there explicitly. If you transform the Ebenecio-Hamiltonian into an approximate form with dedicated contributions for, for instance, electron-phonon coupling, you see it appearing as a term. But that is again analysis and not the starting point, the intrinsic Ebenecio-Hamiltonian. We also looked at the wave function, another ingredient of the Schrodinger equation. And here I asked you if we have two spinless particles, what is the domain and the target set of the wave function? So it is a function, so you need a domain and a particular target set. And most of you found, well, almost everybody found that it was answer C of the four possibilities that I had shown. Why? You start in answer C from R6, so six real numbers, and these are the three position coordinates for each of the two particles. They are spinless, so there should not be a coordinate for the spin degrees of freedom, only for the position degrees of freedom. So you can specify the system by six numbers, six real numbers, and the wave function maps this to a complex number, not necessarily a real number, it is the modulus squared of the wave function that will be a real number, but the wave function itself goes to a complex number. So from R6 to C, this is the domain and the target of the wave function for two spinless particles. And the third ingredient was the total energy, E, which is the energy you need to bring your crystal from the ground state until a state where all electrons and all nuclei are at infinite distances from each other and are at rest. Which means that that total energy is an observable, measurable quantity. If you put a crystal at zero Kelvin, and then measure how much energy you have to put in until you bring it to that particular final state, well, that is the experimental value of the E in the Schrodinger equation, which, as you can see in that comment, is for some people something they didn't realize before. As is written there, especially for physicists, you are so used to write down the Schrodinger equation and you almost mindlessly put E there, without always realizing what that E really means, and even without realizing that it is a measurable property. Okay, that was the Schrodinger equation. Before we move on to the Born-Oppenheimer approximation, let's see whether there is something in the chat. No questions yet, but feel free to put questions there. Good, Born-Oppenheimer approximation, also quite clear for most of you. The confidence bars are heavily weighted to the right. Here I asked you in which situations would it not be valid to make the Born-Oppenheimer approximation. Why that question? The Born-Oppenheimer approximation is very often made. I think more than 99% of all applications of quantum physics in computational physics are with the Born-Oppenheimer approximation, and therefore we do not easily realize anymore what is outside, where would it not be justified to make that common approximation. Let's hunt for that. And most of you followed this reasoning. In order to come to the Born-Oppenheimer approximation, we assumed static nuclei, and therefore the approximation will not be valid when the nuclei move. So we have to find situations where the nuclei move. What are your suggestions? Somebody said, well, if we deform a metal, we squeeze it, or we try to pull it apart, then the nuclei are moving. And then Born-Oppenheimer would not be valid. Well, no, that's not a correct example. Because if you deform a metal, the nuclei do move, but they move slowly, and electrons very rapidly, within picoseconds or less, adapt to the new positions of the nuclei. So you can always describe this as a snapshot of nuclear positions that are always in immediate equilibrium with their electron clouds. So at any moment, Born-Oppenheimer is still valid. Another attempt, the Born-Oppenheimer approximation is not valid when we try to calculate rotational and vibrational states of a solid. Rotational is not so relevant for solids, that's more for molecules, but vibrational states, if we have the nuclei oscillating, so then they are moving. But just as for squeezing a crystal, the motion of vibrating nuclei, although that is a faster motion, the speed of the nuclei is higher than if you deform the material, but still that is, relatively to the speed of the electrons, a very low speed, and therefore the electron system will always immediately be equilibrated. So that is not an example of failure of the Born-Oppenheimer approximation. Some people try electron-phonon coupling, and yes, I don't deny that there can be situations where this cannot be treated within the Born-Oppenheimer approximation, but still, what is electron-phonon coupling? It is an impact on the properties of a material, on electronic properties of a material, based on the motion of the nuclei. And because it is related to phonons, so to nuclear vibrations, these are often slower, slow processes, and even in situations where the electron system clearly reacts on the new positions of the nuclei, so there is an impact of the electronic properties depending on the instantaneous position of the nuclei, even then, that usually happens at a sufficiently low speed, and the electron system will always be in equilibrium with the nuclei. That equilibrium at one snapshot of the nuclear positions may have different properties than the equilibrium at another snapshot, that is when electron-phonon coupling manifests itself, but you can describe it with these static snapshots, you can describe it within the Born-Oppenheimer approximation. We keep searching for examples, other people try temperature. When do we have nuclei that move fast? At high temperature. The higher the temperature, the faster they move. So this is another way to describe the impact of phonons. But even at higher temperatures, for a solid, the nuclei are still moving relatively slow with respect to the electrons. If you would like to reach nuclear speeds that are similar to the electron speeds, you would need temperatures that are so crazily high that your crystal instantaneously evaporates. So if you stay within the crystalline state, as we do here, that regime will never be reached. Someone else tried the opposite reasoning. We need not necessarily high speeds of the nuclei, but we need similar speeds of the electrons and the nuclei. So let's therefore cool the system down close to absolute zero to freeze the motion of the electrons. Well, that would be valid in classical physics, but not in quantum physics. At zero Kelvin, electrons that are in their ground state orbitals, they still move close to the speed of light. That is an equilibrium state. They do not need additional energy from thermal heat to do so. If they stay at zero Kelvin until the end of the lifetime of the universe, they will keep orbiting their nuclei close to the speed of light without the need for any extra energy. So also that will not lead to something where the Born-Oppenheimer approximation fails. So many, many examples of situations where Born-Oppenheimer is still valid. When would it then fail? Well, for instance, the reasoning was correct. We need nuclei that are moving as fast as the electrons are moving. And in order to achieve that, if that is achieved, then the electron system will not be in immediate equilibrium with the nuclear system. But how do we get the nuclei moving at that high speed? An example is ion implantation. If you take an accelerator to accelerate a charged atom, so an ion, to a very high speed and you shoot that into a crystal, then that fast-moving nucleus can reach speeds that are comparable to the electron speed. At every point in the trajectory of that nucleus throughout the crystal, it will not be in equilibrium with its electron cloud. Also, very short-lived transition states in chemical reactions, transition states that live maybe only for a femtosecond, well, that femtosecond is too short to have the electron system equilibrated. And therefore, in transition states, something can happen that you couldn't predict from normal chemistry. You have more degrees of freedom because you cannot make the Born-Oppenheimer approximation, you have to consider nuclei and electrons together. Or, ultra-short experiments. If you have a laser pulse that interacts with a solid and the laser pulse is only a femtosecond or an attosecond long, there will not be time for equilibration. It can kick the nuclei in a very short moment and the electrons cannot immediately adjust. So, this is the first class of situations where Born-Oppenheimer can fail if we can make the nuclei moving fast. This is an example that one of you described, very intense laser fields or magnetic fields, especially if they are pulsed to very short durations. Or, if we leave the solid, I said you can bring the temperature so high that the nuclei get enough kinetic energy, it will not be a solid anymore, you have a plasma. So, if you would go to a fusion reactor where you have a plasma at millions of degrees Kelvin, if you want to describe that plasma by quantum physics, it must be done without the Born-Oppenheimer approximation. A second category, it's called number three here, number two will follow hereafter, but the second category of failure of Born-Oppenheimer is when the nuclei that are involved are very light. And the lightest nucleus you can have is the hydrogen nucleus, which is about 2000 times heavier than the electron, still 2000 times, that's still something, but it's the lightest you can have. And if there is any situation where the nucleus is sufficiently light in order to show quantum behavior itself, just as the electrons do, then it is in situations where hydrogen is involved. And a few people made that suggestion, if you go to very light nuclei, or to situations where the relative masses between nuclei and electrons are not too different, then you can have a situation where Born-Oppenheimer does not apply. So everything that involves hydrogen, we have to be careful. And the third and last category is when you have degenerates, degeneracies in the system. So here I have a cartoon of the total energy of some quantum system, where total energy means the energy of the electrons and nuclei together, so it's really the entire system. And imagine now a situation where you have a double well, so two local minima, that are almost identical in energy. In one of these minima you have one set of nuclear positions with an electron system that is in equilibrium with it, and in the other minimum you have another set of nuclear positions, again with the electrons in equilibrium with that other nuclear position set. But in the two situations that total energy is nearly the same. Well, what will a quantum system that has these properties do? If it cannot decide, based on energy, which of the two situations is better, it will fluctuate between the two, depending on the height of the barrier that needs to be overcome to go from one situation to the other. But if that barrier is sufficiently low, the system can jump, back and forth, between these two situations. It can even tunnel through the barrier, and your system can instantaneously change from one configuration to the other configuration. And if you would see that as a movie, where you focus on the nuclear positions, it would look like some nuclei in your system randomly jump without passing in the positions in between, randomly jump from one position to another. And I think you can feel that such a situation where the position of the nucleus is not strictly defined, that it is hard to describe that with Born-Oppenheimer, where you have to tell what is the position of the nucleus. So that too is a situation where it fails. This completes our discussion of the Born-Oppenheimer approximation. We build further on the tools we will need to develop in the coming week DFT. And we do that by visiting another family of methods, that is in some sense equivalent to DFT, that is often used in quantum chemistry, but that we will not use in this course. So we just give a very brief view on what the Hartree-Fock method and especially the post-Hartree-Fock methods that are built upon this, what these are. And you have seen the story where you conceptually build post-Hartree-Fock. And that sometimes leads to questions, not this year, but this is a good question that I kept from previous years, a question that may be asked by people who have more a quantum chemistry background. And the question is, well, you have the Hartree-Fock ground state, which is a single Slater determinant, and that is not the, the ultimate solution. The ultimate solution is often not, well, is always not a Slater determinant, so it will be outside that blue set. And you have methods in quantum chemistry, the CI methods, configuration interaction, where you build sums of many Slater determinants, you use them as basis functions to approach any solution, including the exact solution. And the question here is, if you do that, by taking sums of excited states Slater determinants, will you then for sure end up at the exact ground state, or is there still something missing? Is the full configuration interaction procedure, that what has just been described here, or does that need something else? And the answer here is, it is sufficient. The set of excited states Slater determinants is a basis for all anti-symmetric wave functions, and that means that you can describe any function, any wave function, as an infinite sum of excited states Slater determinants. So there is nothing more needed for full CI, but of course this is a computationally very expensive procedure, because you need to work with very large basis sets, and therefore we can not always and often not reach that exact solution. In the coming week we will make a short comparison between the advantages and disadvantages of Hartree-Fock MDFT, and speed will be one of the criteria that will be examined. Then we come to the external potential, ingredient after ingredient. The external potential, which is a part of the Hamiltonian, we can write the ab initio Hamiltonian in a way that this external potential is isolated, appears as a sum over different terms, and in order to get a better feeling for what that means, I ask you to write that external potential for a simple quantum system, the O2 molecule. And, well, you have seen for yourself, from the feedback that was available after you had submitted your answer, that you have different ways how to give that answer, but one of them, the most intuitive one, is summarized here on the slide. You have your external potential as a sum of two terms, namely for two nuclei, the two nuclei in the O2 molecule, the rj are the position coordinates of these two nuclei, and the vector r is the position of an electron, so depending on how far away the electron is from the nucleus, that has a charge plus eight electron charges, or an absolute value of plus eight electrons, because it's an oxygen nucleus, that would be the Coulomb interaction between an electron at that position and these two nuclei. That is the external potential for that system. And that defines the quantum system, which is something once you have understood, that it looks very obvious, that is the way how somebody commented upon this a few years ago, but once you realize this, this is very powerful. The only place in your Hamiltonian where you can really see with which quantum system you are dealing, is in the external potential. Once you know the external potential, your quantum system is defined. Everything else is then universal, you only need to bother, if you want to study one quantum system with respect to another one, you only have to bother about the external potential. That will play an important role in the construction of the DFT formalism that you will look at in the coming days. And here is, just in case you missed it, this is the document with the feedback on this exercise that you can download from the website once you have submitted your answer to it. The last ingredient that we need is the electron density, and that is something that we also apply to that simple system, the O2 molecule. Let's assume we have the electron density of the O2 molecule, so the number of electrons per unit of volume as a function of position in space. In order to understand, or in order to test do I understand that concept or not, I ask the question if you integrate that electron density over all available space, so the entire universe, what will be the result of that integral? And there were a few numbers given, for which most people took 16 as the answer, and quite some people also took 1 as the answer. The correct answer is 16, because if you integrate a density over all space, you should find the absolute number of what you have integrated. There are 16 electrons in the O2 molecule, the density gives the probability to find a particular number of electrons in a given volume, so if you have everything, you must have 16 electrons. Why do some people give 1? That's a contamination of working with wave functions, wave functions that are probabilities, they are often normalized to 1, but if it is an integral over a charge density, so that's not a wave function, that's a charge density, then it's the total charge that should result. Either a wave function normalized to 1, you have the total probability, 1 or 100% if you integrate, or a charge density, you integrate over space, you have the total charge, here 16 electron charges. Okay, that was a quick run through everything you did in the past week, let's now first do, just as last week, five minutes in which you can give your one paragraph summary of the past week, and a proposal for an exam question. Later today, I will upload the answers that you have given last week, and that will be put under the video of last week, because in the past week, the people who did not watch this live, they should also have time to contribute this, so therefore, this comes always with one week delay, but please now fill out in the form your contribution, and after these five minutes, we will have a quick look at the situation for the project. Thanks for your contributions, there is not really something to tell on the hands-on part, so I assume that you have installed the software by now, and that you are able to run it, I didn't receive extra questions in that respect in the past week, should there still be issues for someone, then please post it on Zulip, and we can try to find a solution. For the project, what is the situation there? About 25 people have signed up for the project, that's a sizeable number, so that means we can form something between six and nine teams, depending on some details, like there are people who have suggested topics that they are personally interested in, and that may affect the size of the different teams, so I will make today or tomorrow the team configuration, and that will be emailed to all of you who signed up for the project, so you will know very soon in which team you will be. And that was basically it, so next week we will look at the second part of the DFT topic, and that means now, with all the ingredients that we have, let's now construct density functional theory, and in the hands-on part, we will look at what we will call convergence testing, a very important practical numerical step that needs to be done at the start of every new series of calculations. That's it from my side, I will now go back to the chat and wait for one more minute to see whether additional questions appear there, there was not much activity in the chat, which I assume is an indication that everybody is following well, but should there be questions about the past week that have not yet been addressed, then you can put them here. Okay, I don't see anything, so I will leave you here, and we will see each other again next week, same place, same time. Bye bye!