

student summaries and exam question suggestions

Density Functional Theory (part 2)

*These pages contain student summaries for the module **Density Functional Theory (part 2)**, as well as student suggestions for exam questions on this module. You can use these pages as a study help for this module. The summaries can help you to see the highlights of this module from different points of view. The questions can challenge you to think about the content. If you take the exam, then some of the questions suggested this year will be included in the exam. The contributions suggested this year are **are printed in color**. The ones in black were contributed in previous years.*

1. student summaries

- The convergence testing is an important aspect in finding the correct value for any parameter that you want to calculate on your material.
- The two central theorems, and its relation to the Kohn-Sham equations. What is the exchange and correlation functional and why is needed.
- DFT is a computational method. It does not calculate wave functions but it uses electron density which contains all the information of the structure. The calculations can't be done analytically, so must be done numerically by using computational algorithms and approximations.
- What the importance of the exchange correlation function is, what information it contains and how the presence of this function sets DFT apart from other methods of solving the Schrödinger equation numerically.
- First key insight is that the ground state electron density uniquely maps to an external energy. The 2nd HK-theorem does explicitly stand by itself because it does provide the understanding that the variational principle applies to the densities, which the 1st theorem does not explain.
- The amazing implications of the first Hohenberg-Kohn theorem: both its meaning as well as its consequences.
- Hohenberg-Kohn, theorems, Kohn-Sham equation, exchange-correlation functional, Jacob's ladder, numerical solution methods.
- Hartree-Fock vs DFT
- The two Hohenberg-Kohn theorems and why they make DFT possible. Then the Kohn-Sham equations and how they are used to obtain a solution.
- The information about both Hohenberg-Kohn theorems. The exchange-correlation functional
- From the first HK theorem we know that the ground state electron density uniquely determines all observable properties of the system. From the second HK theorem we know that the ground state energy functional is minimized when the ground state electron density is used as input. The Kohn-Sham scheme is a practical method of implementing DFT. It turns our many-body problem into the computationally simple problem of solving a set of independent particle equations. We need to make sure all our DFT calculations have converged, convergence of the hydrostatic pressure is a good indicator of convergence.
- The HK1 and HK2 theorems define the existence and the form of the Exchange Correlation Functional. The pseudo-potential-Plane wave method helps to reduce the complexity of the problem but smoothening the potential near the nuclei.
- Meaning of first and second HK-theorems, basic meaning of "self-consistency problem", understanding what is "correlation" with help of solar system analogue
- consequences of both theorems and the concepts of exchange and correlation
- The role of the exchange-correlation potential in description of the energy of the system.

- the Kohn-Sham theorems state that 1) you can do quantum physics with the ground state density, which has all the information you need about the system, 2) you can find the ground state density by minimizing the energy of the system with a self-consistent method. DFT is an approximate solution, because you don't know the exchange and correlation functionals, which are basically the terms in the KS Hamiltonian to account for the fermionic nature of electrons (exchange) and the electron-electron interactions (correlation). It is possible to think about higher approximations which will make the prediction better (Jacob's ladder). Besides the theoretical approximations, there are also numerical considerations to take into account because of the nature of KS equations. These equations express the density as an expansion into non-interacting pseudoparticles, which might also be expressed as linear combinations of an infinite basis set of functions. These considerations reduce the KS equations (differential equations) into a linear algebra problem, where the final result are the coefficients of the expansions. Numerical approximations are defined for the amount of functions to consider in the basis sets.
- The 1st H-K theorem says that quantum mechanics can be done without wave functions. All observable properties can be obtained from the ground state electron density - a real-valued function of 3-dim real argument. The 2nd H-K theorem says that the functional that gives the ground state energy of the system has a minimum, and that this minimum is achieved when the function is the true ground state electron density function. In practice, DFT is done within the Kohn and Sham framework (although, it does not have to be so) in which the system of many interacting particles is replaced by a system of non-interacting quasi-particles each of which is put into an averaged potential of all other particles plus an exchange-correlation functional that is unknown and should be guessed. There is a need for a different definition of correlation in classical systems and in quantum systems because in the case of quantum particles there's an extra exchange energy that needs to be taken into account. There is no exchange energy in classical systems.
- At the fundamentals of DFT are two theorems. The first HK theorem states that there is as much info about a system in its density function as in its wave function, so that wave functions are not needed for calculations. The second HK theorem says that if the ground state density is inserted in the total energy functional the corresponding total energy value is minimal. A practical recipe to calculate material properties via DFT is given by the method of Kohn and Sham. They give an expression for the density function of a system, introducing a new entity: the exchange correlation functional. This functional is not known, but approximated by several different expressions of which the LDA the most simple is. Exchange and correlation energies must be included to account for the error that the KS method makes when assuming that the many-body problem can be divided into a set of distinct single-particle problems. For the actual numerical calculations a set of basis functions is chosen to describe the single-particle wave functions that are used to determine the density function of the system. By doing so, the problem is reformulated into a matrix algebra problem, which can be solved.
- Both HK theorems, the working principle of KS method, how to get the density, difference between correlation and exchange and the difference between HF and DFT
- The importance of the HK theorems and the recipes needed for the different methods HF vs DFT to get an approximate density. What the XC-functional is and how it can be used in combination with the meaning of both contributions of Exchange and Correlation.
- Firstly the two HK-theorems and their implications, they give a starting point for DFT. Next of course the Kohn-Sham equations. Then the XC-functional and how to work with it without actually knowing what it looks like. Also the concept of correlation is very important.
- Actually, the last summary given in the class seems appropriate: we remember the HK theorems and most importantly the (quite simple) interpretation and results of that. Also we know that in practice, we keep in mind those theorems by looking for a solution for the density with the KS equations. Also, we defined more in detail the differences between post-HF and DFT, especially regarding exchange and correlation energy.
- The concept of exchange and correlation energies, the HK theorems, the difference between HF method and DFT.

- The two HK theorems: The first one to express there is one-to-one (bijective) relation between the external potential of a system and the corresponding (ground-state) electron density of that system. For every property of the system there exists a functional where we can plug in the density and find the property value. The second expresses that the functional that returns the total energy has a minimal value when the ground state density is plugged in, thus providing a 'practical' way of finding this ground state density. A DFT is then anything based on the KH theorems. One practical method to find the ground state density is the method of Kohn and Sham. This method uses the Kohn Sham equation $H_K S * \phi_i = \epsilon_i \phi_i$. Solving this equation is equivalent to solving the Schrödinger equation, but has much simpler mathematics because energy of a (quasi-)particle in the potential generated by all the other particles in the problem (iii) a term because of the exchange correlation functional. As soon as the XC functional is determined the equation can be solved exactly, however, for now not GGAs. When comparing the (post) Hartree-Fock method and DFT, in practice DFT will be used for larger systems because of the computational cost of HF.
- The "Density" and "Functional" parts of DFT are based on the two Hohenberg-Kohn theorems. The first theorem states that there is a one-to-one correspondence between the ground state density of a many electron system and the electron density. The most important consequence of this theorem is that observable ground state properties can be expressed as a unique functional of the electron density, instead of using the for us more familiar wave functions. The second theorem provides a method to find this ground state density by saying that the ground state density minimizes the corresponding energy functional ($E(\rho)$).
 The method of Kohn \ Sham translates the many-body schrodinger equation of the molecule or solid to a single-particle equation: $H\phi = E\phi$, where the ϕ are single particle wave functions. To get an exact one-particle equation for the electrons (quasi-particles) the hamiltonian is split in the kinetic energy of the electron, the external potential coming from the nuclei, a Hartree term that can be interpreted as a static and average distribution from all other electrons (quasi-particles) and an exchange-correlation potential correcting for the assumptions made in the Hartree potential. A perfect universal XC-functional would result in exact solutions, but this functional is not yet known. One of the possible guesses for this functional is the Local Density Approximation (LDA).
 Since the electron density is used to construct the Hartree potential and since it is also the object that we are looking for, the K-S equation must be solved iteratively until self-consistency is reached. For the one-particle orbitals ϕ a suited set of basis functions has to be chosen.
- The First Hohenberg-Kohn theorem states that there is a one-to-one correspondence between the ground state density of a many-electron system and the external potential. The second theorem states that the unique functional that returns the ground state total energy when applied to the ground state energy density, returns a higher energy for any other density. Most DFT uses the Kohn-Sham equations. In these equations, the Hamiltonian has the following contributions: Quasi-particles with kinetic energy; Subject to Coulomb potential of nuclei; Interacting with the average, static distribution of all other quasi-particles; Subject to the effect of an 'exchange correlation' potential. We can make the local density approximation, which postulates that the exchange-correlation potential of a solid with a density ρ , is represented by the pointwise contributions of a jellium with locally the same densities as encountered in the solid. This "guess" leads to very reasonable predictions. Furthermore, it is computable, so that the DFT becomes useable. The Hartree method assume that the wave function is the product of the single-particle wave functions. The Hartree-Fock method assumes that the wave function is a Slater determinant. The exchange energy is the difference between the Hartree and the Hartree-Fock solution. The correlation energy is the difference between the Hartree-Fock solution and the exact solution. DFT will typically be used for large molecules as it is easier to compute. Solutions are usually achieved by using the basis set method in combination with reciprocal space.
- The methods that are available for us, do not give the exact solution. We should use the XC-functional to find this solution. Hartree-Fock and DFT methods can be used to calculate quantum mechanic properties of materials. HF is the preferred method since it gives the best results but, in case of very large molecules, the calculation time can increase significantly. In this case, it is more convenient to use DFT. In order to find the solution of a calculation, an iteration scheme is used that finishes when the obtained solution resembles the old solution within a preset margin.

2. exam question suggestions

- What is the second Hohenberg-Kohn theorem? Is this theorem a trivial consequence of the first theorem?
- What is the exchange and correlation needed in order to make calculations within DFT?
- What is the main principle of Density Functional Theory (DFT), and how does it differ from traditional wavefunction-based quantum mechanical methods?
- What is the benefit of rewriting the schrodinger equations into the KS equations, and in this formalism what information is contained in the exchange correlation function?
- What exactly is correlation exchange energy? What are the steps of the Jacobs ladder?
- What do the 'X' and 'C' in XC-function mean? Explain what they represent.
- What is the meaning of exchange-correlation functional in the Kohn-Sham equation?
- How we differentiate Hartree-Fock and DFT
- As in the HF vs DFT section which method would you use for a specific molecule and why?
- Explain the first Hohenberg-Kohn theorem in your own words
- What is the difference between the correlation energy and exchange energy
- How would you determine the pseudo-potential to be used? If a nodeless orbital contributes to the electron density outside the muffin tin sphere?
- Formulate the first and second HK theorems with your own words
- Explain the role of the exchange potential - how does it differ from classical systems, and how it differs from correlation energy.
- Can you access the excited states of the system given you know the ground state density ?
- First H-K theorem implies that the ground state energy of the system can be written in the form $E[\rho] = T[\rho] + U[\rho] + E_{\text{ext}}[\rho]$, where ρ is the ground state electron density, T is the kinetic energy of the electrons, U is the energy of electron-electron interactions, E_{ext} is the external potential. Which of the three terms depends on the solid or molecule you are studying, and which terms don't depend on a particular solid or molecule?
- Describe why we need an exchange correlation functional in the Kohn-Sham hamiltonian and how it is expressed.
- What are the first and second HK theorems? Explain them.
- What's the advantage of HF over DFT concerning their possibility to get exact results. Thus name an advantage and a disadvantage of both DFT and HF.
- Explain the concept of correlation with an example and how the XC-functional incorporates correlation.
- Explain why the LDA approximation works well, although it seems quite simple.
- Explain in your own words the difference between the correlation and exchange energy.
- How do we solve the self consistency field problem when solving the KS equation?
- Why would you use the Post-Hartree-Fock method if possible and under which circumstances would you opt for regular Hartree-Fock or DFT?
- Explain the exchange-correlation potential and the Kohn-Sham equation.
- Explain the two Hohenberg-Kohn theorems.