# student summaries and exam question suggestions
# *DFT (part 1)*

*These pages contain student summaries for the module* **DFT (part 1)**, *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

- It is good to know why we use all these other kind of methods and not just solve it analytically. That is because it is impossible to know for sure what the energie and interacting energy is going to look like.
- The background of DFT, specifically what the D (density), F (functional) and T (theory) mean. Another important part is the BO-approximation and when it becomes invalid.
- What a functional is, the difference between the wave function and electron density, the different parts of the Schrödinger equation and what they are, what the BO approximation is and when it holds.
- The form of the Schrödinger equation and how it is simplified, the definition of the electron density and the concept of a functional
- Essential definitions as: charge density, external potential and BO-approximation.
- I think the principles behind DFT and the assumptions we make in this formalism are the key aspect of last week. While they were still very theoretical at this point they will become more important to understand and set up the calculations later.
- First and foremost it is essential to remember that the system can be described by the electron-nuclei interaction term. Furthermore, I think it is important to remember the edge cases of when BOA does not apply respectively when it fails e.g. laser experiments.
- The Born-Oppenheimer approximation is a good approximation for the most cases.
- The most important things from this week are the Born-Oppenheimer approximation and the concepts of the external potential and the electron density.
- I think the physical meaning of the energy in the Schrodinger equation, and the fact that it is a measurable quantity.
- For DFT, the subject of study are electrons, but not as individual particles, but rather as a variable density. This density becomes the main problem and it is simpler to solve (because remains in the real domain) compare to individual solutions for each electron.
- For this week, I acknowledged that the external potential, wave function and density function is injective to each other, and I realized that I need to regard questions from quantum mechanics which the external potential is a operator (so amazing)
- That DFT uses the BO approximation. That the external potential is unique for different systems, therefore it defines the used system. (Post)-H-F methods are also an possible method, but much less used in the field op materialphysics. More so in chemistry.
- Schrodinger Equation Born Oppenheimer Equation and Hartee fork Method
- That both DFT and hartree fock fundamentally start with the BO approximation, where DFT is centered around the electron density and hartree fock around the slater determinants to find an approximate wavefunction. post hartree fock theoretically gives an exact solution, but requires more computation time as the precision increases.

- The different parts of the Schrödinger equation, the information about the Born-Oppenheimer approximation and the electron density
- 1. The Schorödinger equation 2. Born-Oppenheimer approximation 3. The external potential
- - The external potential - The physical meaning of the energy in the Schrodinger equation - Born-Oppenheimer approximation and invalidity - (post-)HF methods
- In the beginning of this lecture the definition of functions and functionals was given. The difference between the two was then discussed and clarified with some examples. Then the different parts of the Schrodinger equation were discussed. Next an often made approximation was discussed namely the Born-Oppenheimer approximation and its validity was questioned. The operation of (post) Hartree-fock methods was explained and the link with Slater determinants was made. After this the different interaction terms were discussed and the external potential was indicated. Finally the concept of electron density was clarified. Two subjects that are essential to understanding DFT.
- The difference between a function and functional + example. Components of schrodinger equation. BO approximation with its caveats. What Hartree Fock actually does. How to get the external potential. The meaning of the electron density.
- about fundaments of DFT, energy concept, slater deteminant concept
- The concept of observables, especially linked to the total energy and electron density, should be remembered. Some expertise in expanding a system's Hamiltonian and identifying the (external) potential(s) therein would too be a worthy take-home message.
- The meaning of the total energy E in the Schrödinger equation and the external potential
- To know about the properties of a material we should solve the Schrodinger equation that describe the system of this material which is composed of electrons and nuclei. to do so we start by analyzing the hamiltonien of the system which is composed from: the kinetic energy of electrons, kinetic energy of nuclei, electrons-elecrons coulomb interaction,nuclei-nuclei coulom interaction and elecron-nuclei coulomb interactions. It‘s impossible to deal with a similar hamiltonien as it contains 5 different components filled with many parameters and as much as we increase the number of atoms and nuclei in the system as much as the system gets complicated and impossible to solve. To facilitate the process of solving the equation we apply some approximations like the Born-Openheimer (BO) approximation where we suppose that the nuclei at rest and the mass of nuclei is so much bigger than the mass of electrons what slows so much the motion of the nuclei compared to electrons, therefore we can eliminate the kinetic energy of nuclei (The kinetic energy of nuclei is proportional to its speed). The interaction nuclei-nuclei term is constant so we don‘t have to deal with it in the equation as it will stay unchanged. Consequently you will notice that the only term where the nuclei appear in the hamiltonien after the application of BO approximation is the nuclei-electrons coulomb interaction. this term is called the external potential, produced by the nuclei so the electrons of the system have to adapt to it. Another term that appears in the Schrodinger equation is the energy E which is the difference between the ground state energy of the system at 0 Kelvin and the energy of the exited state where the electrons and nuclei are in infinite distances from each other.
- Schrödinger equation of solids have Coulombic and Kinetic energy interactions between nuclei and electrons which form a many body system. The interactions in solids for each atoms are so many that there is a need for making certain assumptions, such as Born oppenheimer approximation and Hartree-fock methods, to get solution of Schrödinger equation in order to calculate its properties.
- The many-body Schrödinger equation is made a little less complex by applying the B-O approximation, i.e. assuming that the nuclei are at rest. Afterwards, The DFT is a method to transform this complex problem (Schrodinger eq.) to much simpler equations which can be solved by a numerical solution method. The (post-)Hartree-Fock methods can also be used to solve the exact Hamiltonian. This Hamiltonian contains the external potential which defines the system we are studying.
- Born Oppenheimer approximation, external potential

- Functionals are "functions of functions" to numbers. The fundamental equation to be solved in this case is the Schrödinger equation. It contains the Hamiltonian, which is every relevant energy term combined, the complex wave function and the total energy, which is a number. To solve this, the Born-Oppenheimer approximation is used: nuclei move way more slowly than electrons and are thus considered "stationary". The stationary positions of your nuclei now define the external potential, which defines your system. Now you can use Hartree-Fock using Slater determinants, or DFT using electron density to solve your problem.

- It is important to remember that 1) a functional maps a function to a number, not a function to another function, 2) the BO approximation is a very good approximation that treats electrons in the field of static nuclei and then nuclear motion in the electronic PES, 3) postHF methods are not tractable for large systems such as solids, and that the external potential is defined by position of nuceli and uniquely defines the system.

- The Hamiltonian used, The Born-Oppenheimer approximation and its limits. The external potential and that it defines the system. Electron density and how to calculate it.

- What a functional is, why the born-oppenheimer is such a good approximation and how the external potential uniquely defines the system.

- The main thing to remember is the difference between Hartree-Fock methods and DFT.

- For me, the essential thing that all student should remember is the "common thread", that is knowing that the starting point is the Schr. equation, that make the BO approximation and than DFT is a method that we will use to solve the system that we get, after having approximated our Sch. equation.

- The Schroedinger equation of a solid can usually be solved using the Born-Oppenheimer approximation. After this step, we can apply Hartree-Fock or DFT methods to further simplify the problem. DFT relies heavily on the external potential and the electron density.

- –¿DFT is based on functionals that map from electron density functions to real-number scalar values of total energy –¿DFT is different from Hartree-Fock and post-Hartree-Fock, which are a different class of methods –¿DFT relies on the Born-Oppenheimer Approximation, which fixes the positions of the nuclei, then uses those positions to calculate an external potential, to which the electrons then respond

- 1. Functionals 2. Injective and surjective – V(ext) to wave fn to density 3. unique functional that returns gnd state total energy when applied to gnd state density only 4. How BO approx saved DFT. 5. Meaning of external potential

- Things to remember: 1) The conditions in which the Born-Oppenheimer approximation is valid. 2) The external potential doesn't depend on the electrons. 3) The electronic density express (integrated over all space) the number of electrons in the system.

- - Which interaction is taken into account in the external potential? - Basic idea of the born-oppenheimer equation. - Energy contributions in Hamiltonian.

- The hamiltonian and wavefunction of a quantum system captures all interactions present in said system. In the BO approximation the nuclei are considered massive, and the electrons form an equilibrium around the nuclei instantaneously.

- Understanding the concepts of Born-Oppenheimer Approx to help solve the schrodinger equation, Terms of the hamiltonian, electron density, external potential, ...

- The measurable energy and what does it mean. The Hamiltonian interactions. The main idea of Born–Oppenheimer approximation and where does it fail.

- A functional takes a function as input and a number as output. The external potential completely defines our electronic system. In ab initio materials modelling there are three levels of approximation: Born-Oppenheimer, density functional (Hartree Fock) and numerical methods.

- It is really important to be able to distinguish a function from a functional, as well as to have insight into which properties will be affected by the Born-Oppenheimer approximation and which ones will not.
- The difference between functions and functionals (functionals transform function to a number). The composition (energy contributions) of Hamilton operator. The principle of Born-Oppenheimer approximation.
- Electron density and approximations
- I will likely remember the BO approximation, even though I don't find it that important. Philosophically, it's an interesting object. We should remember, however, how the external potential works as well as the importance of the charge density.
- The concept of functional, how HF methods works and why they are needed
- Situations where the Born-Oppenheimer approximation fails: only when the electron density is not able to stabilize with respect to the nuclei, the approximation is not valid. This occurs in collisions at high energies (ion implanations) or at very small nuclei masses
- The most important aspects of the Schrödinger equation are the hamiltonian, the energy and the wave function. The hamiltonian (and the argument of the many body wave function) can be simplified via the Born-Oppenheimer approximation, assuming that the nuclei are at rest. The external potential determines the system you're studying and it's called external because it's given, from the point of view of the electron gas.
- The definition of the electon density, definition of a functional, applicability of the Born-Oppenheimer approximation.
- DFT is an exact method if we know the correct EC functional. HF is not exact because it is limited to Slater Determinants and post-HF samples other wavefunctions within the set of antisymmetric wavefunctions. Thus with infinite computation time, post-HF will also be exact.

## 2. exam question suggestions

- Why do we use DFT, and why is the Born-Oppenheimer approximation so important?
- Why does the BO-approximation remain valid, even at high temperatures?
- Explain what assumptions the Born Oppenheimer approximation makes, and justify why this is a valid approximation in almost all casus for ab initio DFT calculations.
- How does the Born-Oppenheimer approximation simplify the Schrödinger equation and when can it be used?
- Why the BO-approximation can be implemented in the majority of standard DFT calculations?
- Is the charge density a function or a functional and why is this the main object of interest in DFT rather than the wavefunction of the electrons from which the density can be calculated?
- Which interactions are considered in the external potential? In which cases does the Born- Oppenheimer approximation fail? Name at least 2.
- Give the expression for the external potential energy in function of the electron charge density.
- When is the Born-Oppenheimer approximation not valid? Give three possible scenarios. Why is it not valid/What needs to be the case for it to be valid?
- Please describe the Hartee-Rock method. Why does a post-Hartee Fock method exist? What does it improve?
- How is the external potential represented for a molecule of two atoms, each with 8 electrons and 8 protons?

- In which cases the Born-Oppenheimer approximation will not work?
- Is the Born-Oppenheimer approximation still valid when a material is undergoing plastic deformation?
- What assumption is implicit being made by using DFT?
- What is Schrodinger Equation for solid. When does born Oppenheimer fail? And How we prove hartee fork method?
- How is the external potential related to the adiabatic approximation
- Describe the different parts of the Schrödinger equation, what changes are made when we use the Born-Oppenheimer approximation?
- Please write out the Hamiltonian of a many-body system containing many electrons and nuclei.
- When is the Born-Oppenheimer approximation invalid?
- Give the definition of a functional and give an example of it.
- Provide 4 cases where we can use the BO approximation, and 4 cases where we can not.
- formulate slater determinant for o2 molecule
- An external potential expression is given for a "simpler" molecule (other than explicitly shown, e.g., N2, NO, H2O...). Which system does this expression uniquely describe?
- Given a certain external potential, deduce the full Hamiltonian
- What are the components of the exact hamiltonien of a system? If you apply Born-Openheimer approximation to it what will be the new hamiltonien?
- Show the Schrödinger equation interactions for hydrogen molecule.
- Why does the external potential identify the system we are studing?
- What is a functional? Give an example.
- Give a set of examples of different functions and functionals and ask "which of the following are functionals"
- Write down the Hamiltonian for a solid and explain each of the terms. What approximation(s) can you make?
- Why does the Born-Oppenheimer approximation almost never fail? And give an example for a situation where it does
- What is the difference between Hartree-Fock and DFT?
- What does the E mean in the Schrodinger equation?
- What is the difference between the electronic wave function and the electron density?
- Please give three examples of a functional (i.e. a mathematical map from functions to scalar values), including one example from Density Functional Theory.
- What exactly is the energy E that we get from solving hamiltonian in schrodinger equation? How is it measured experimentally?
- In which conditions the Born-Oppenheimer approximation is required? In which conditions it fails?
- What is the basic Idea of the born-oppenheimer equation?
- Under what circumstances does the BO approximation fail?
- Derive the external potential of molecule X starting from the general expression of the hamiltonian. What would the integral of its electron density yield?

- when the Born–Oppenheimer approximation fails?
- Define in your own words what the symbol 'E' means in the Schrodinger equation for a solid material.
- In vectorcalculus, the gradient of a three dimensional function f can be determined by multiplying the nabla or del operator with that function (grad f = (df/dx,df/dy,df/dz). It can be used to calculate the normal to a scalair field for a certain point in space. Can you say that a gradient is a functional? Why or why not?
- Define Born-Hohenberg approximation.
- Explain the Born-Oppenheimer approximation based on (with help of) the Hamilton operator - show which terms can be left out, thus simplifying the equation and computational effort significantly.
- Explain the limitation of Hartree-Fock method (the electron correlation)
- Does the charge density "exist?" Is it tangible, measurable, or is it simply a mathematical tool we are using to find an approximative solution? Could we make an analogous DFT approximation for, say, a "magnetic charge density?" Why or why not? Explain.
- Write the entire hamiltonian of a system with 5 nuclei (A, B, C, D and E) and 8 electrons (a, b, c, d, e... i and j)
- Can the Born-Oppenheimer approximation be used at high temperatures, close to the melting point?
- Describe the electron density and explain whether it's a function or a functional.
- Write the electron density operator, and use it to derive the electron density as a function of single particle orbitals.
- When is the born-Oppenheimer approximation valid?
- Given a certain external potential, why is this enough information to identify the system at hand? Identify the system at hand.