بسم الله الرحمن الرحیم

Chapter three

Density functional theory (DFT)

Titels

✓ **Why use DFT?**

✓ **knowing the terminology**

✓ **Density Functional Theory**

Why use DFT?

❖ The purpose is to explain in a non-mathematical way what density functional theory is and what it is used for.

❖ The quantum mechanical wavefunction contains, in principle, all the information about a given system.

❖ For the case of a simple 2-D square potential or even a hydrogen atom we can solve the Schrödinger equation exactly in order to get the wavefunction of the system.

❖ We can then determine the allowed energy states of the system.

❖ Unfortunately it is impossible to solve the Schrödinger equation for a N-body system.

❖ Evidently(مشخصاً), we must involve some approximations to render the problem soluble.

❖ Here we have our simplest definition of DFT: A method of obtaining an approximate solution to the Shrodinger equation of a many-body system.

❖ DFT computational codes are used in practice to investigate the structural, magnetic and electronic properties of molecules, materials and defects.

knowing the terminology

❖ It is reminded some of the ideas used in this field and introduce them to some more.

many-body problem

❖ Take, as an example of a many-body problem, the case of a regular crystal.

❖ The electrons are not only affected by the nuclei in their lattice sites, but also by the other electrons.

Coulomb potential:

❖ Remember, this is just the classical potential that arises from any charged object.

Hartree Potential:

❖ Here we say that each individual electron moves independently of each other, only feeling the average electrostatic field due to all the other electrons plus the field due to the atoms.

❖ In other words, this is the potential due to the electron density distribution and ionic lattice but neglects exchange and correlation effects.

Pauli Exclusion Principle:

This is the rule that disallows two identical particles to lie in the same quantum state.

Exchange interaction:

❖ This is due to the Pauli Exchange Principle.

❖ In this case it states that if two electrons have parallel spins then they will not be allowed to sit at the same quantum state.

❖ This phenomenon gives rise to an effective repulsion between electrons with parallel spins.

❖ Not only, then do we have two electrons interacting via their electronic charge, but also by their spins.

Correlation interaction:

❖ In this case there is a correlated motion between electrons of anti-parallel spins which arises because of their mutual coulombic repulsion. See also Jellium

Jellium

❖ Jellium is the name given to an homogeneous electron gas.

❖ The motion of the electrons in the gas is not only affected by the coulomb interaction between them. There is also a purely quantum mechanical process at work.

❖ The motion of the electrons is correlated by the Pauli Exclusion principle.

❖ The electrons with parallel spins, must maintain a certain separation.

❖ The anti-parallel spin electrons keep apart to lower their mutual coulomb repulsion. So we can gain energy in two ways.

❖ Moving parallel spin electron apart will lower the exchange energy, moving anti-parallel spins apart will lower the correlation energy.

The exchange-correlation hole

❖ The exchange-correlation effect gives rise to an exchange-correlation hole around each electron in the gas. The hole is just the exclusion radius caused by the Pauli exclusion principle.
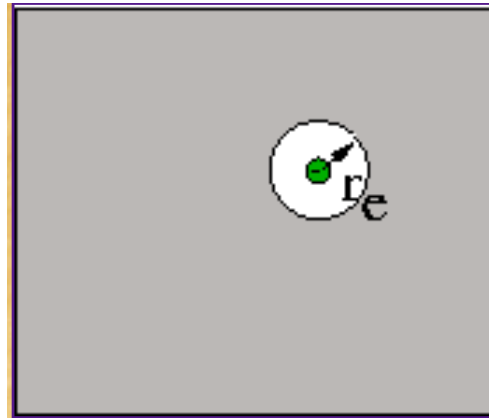
❖ The radius of the hole corresponds to the exclusion of a single electron thereby giving the hole a single positive charge.

❖ The overall charge of the quasiparticle (the electron and its exchange-correlation hole together) is zero.

❖ Of course in reality, there is no marked boundary for the exclusion zone as drawn, the boundary is diffuse.

Now that you are familiar with the terms involved, here is an example of a widely used method for solving the many-body problem.

Hartree-Fock:

❖ This method employs the Hartree potential but also forces the exchange interactions by forcing the antisymmetricity of the electronic wavefunction.

❖ This acts to lower the total binding energy of atoms by ensuring that parallel spin electrons stay apart.

❖ The downside (نقطه ضعف) to the theory is that it neglects correlations in the motion between two electrons with anti parallel spins.

Density Functional Theory

❖ Firstly we need to reduce as far as possible the number of degrees of freedom of the system.

❖ Our most basic approximation does just this. It is called the Born-Oppenheimer approximation.

The Born-Oppenheimer Approximation

❖ Since the ions are so massive in comparison to the electrons, the kinetic energy of the ions is much smaller than that of the electrons.

❖ This idea forms the basis of the Born-Oppenheimer approximation.

❖ The electrons are assumed to respond instantaneously to the motion of the ions.

❖ A functional is a function of a function.

❖ In DFT the functional is the electron density which is a function of space and time.

❖ The electron density is used in DFT as the fundamental property unlike Hartree-Fock theory which deals directly with the many-body wavefunction.

❖ Using the electron density significantly speeds up the calculation.

❖ Whereas the many-body electronic wavefunction is a function of 3N variables (the coordinates of all N atoms in the system) the electron density is only a function of x, y, z -only three variables.

❖ Of course (مطمئناً) simply doing any old calculation fast is not good enough - we also need to be sure that we can derive something significant from it.

- It was *Hohenburg and Kohn* who stated a theorem which tells us that the electron density is very useful.

- The *Hohenburg-Kohn* theorem asserts that the density of any system determines all ground-state properties of the system.

- In this case the total ground state energy of a many-electron system is a functional of the density.

- So, if we know the electron density functional, we know the total energy of our system.

- By focusing on the electron density it is possible to derive an effective one-electron-type Schrödinger equation.

❖ We can now write the total energy of our system in terms of which are all functionals of the charge density. These terms are:

✓ Ion-electron potential energy

✓ Ion-ion potential energy

✓ electron-electron energy

✓ electron kinetic energy

✓ exchange-correlation energy