The following note is based on the 2nd edition of *Computational Materials Science: An Introduction* by **June Gunn Lee**

▾ Chapter 5: Density Functional Theory

Electron density:

Electron density $\rho(r)$ is the number of electrons per unit volume at a given point r. The corresponding operator is defined as:

$$\hat{\rho}(r) = \sum_i^n \delta(r - r_i)$$

$$\rho(r) = \sum_i^n |\phi_i(r)|^2 = 2 \sum_i^{occ} |\phi_i(r)|^2$$

where ϕ_i are the Kohn-Sham orbitals (discussed later). If the wavefunction is normalized to unity, integrating $\rho(r)$ over all space will give us the total number of electrons:

$$\int_{\text{all space}} \rho(r)\, dr = n$$

Hohenberg-Kohn theorems:

Theorem 1: *The external potential is a unique functional of the electron density.* That means for a many-body system the electron density alone can give us external potential, and consequently, the Hamiltonian, wavefunction and other gorund state properties.

Theorem 2: The ground state is the global minimum value of the energy functional of the system in terms of electron density, i.e., the $\rho(r)$ which gives the global minimum value of $E[\rho(r)]$ is the ground state electron density.

Kohn-Sham approach: In the HF approximation, we saw that:
$$E = E_k + E_{ext} + E_H + E_x$$

What Kohn & Sham did is to decompose this interacting many-body energy into the energy of many non-interacting one-body energies. So the total kinetic energy now:
$$E_k = E_k^{non} + E_k^{int}$$

Also they introduced a new correlation energy E_c^{int} for the interacting electrons where it accounts for the correlation between different spin electrons in the interacting many-body. So, the total energy is:

$$E = E_k^{non} + E_k^{int} + E_{ext} + E_H + E_x + E_c^{int}$$

We can simplify this by introducing *exchange-correlation energy* term

$$E_{xc} = E_x + E_c = E_x + E_c^{int} + E_k^{int}$$

So, the final form is:

$$E = E_k^{non} + E_{ext} + E_H + E_{xc}$$

Energy terms:

- *Kinetic energy:* for an interacting system, kinetic energy is given as $\langle \psi | \hat{T} | \psi \rangle$ where $\hat{T} = -\frac{1}{2}\nabla^2$ is the kinetic energy operator. Hoewever, here in KS approach, the E_k^{non} is given by the KS orbital product: $\langle \phi | \hat{T} | \phi \rangle$ as a summation. This energy can be obtained by relating it to electron density by assuming it as a system of homogeneous electrons.

- *External energy:*

$$E_{ext}[\rho(r)] = \int U_{ext}(r)\rho(r)dr$$

- *Hartree energy:*

$$E_H[\rho(r)] = \int U_H(r)\rho(r)dr = \frac{1}{2}\int\int \frac{\rho(r)\rho(r')}{|r-r'|}\,dr\,dr'$$

- *Exchange-correlation energy:* This is the new term we get in KS approach. Even though this is the smallest contribution of energy, this determines many of the key factors. It is usually approximated by various method.

In conclusion: Hartree approximation lacks the exchange and correlation energy, HF approximation incorporates exchange energy but lacks correlation energy, and lastly, KS approximation incorporates both exchnage-correlation energy. The better we approximate the XC functional, the better or DFT result will be.

Kohn-Sham equation: In KS approach, we minimize the system energy with respect to the KS orbitals in order to obtain the orbitals that give rise to the ground state energy (HK theorem 2). These are Schrodinger-like equations:

$$\left[-\frac{1}{2}\nabla^2 + U_{ext} + U_H + U_{xc}\right]\phi_i(r) = \hat{H}_{KS}\phi_i(r) = \varepsilon_i\phi_i(r)$$

where $\hat{H}_{KS}$ is the KS Hamiltonian, ε_i are the KS eigenvalues and $\phi_i(r)$ are the KS orbitals. By solving KS equation, we can get the KS orbitals.

The physical significance of KS orbitals and eigenvalues are not clear (yet).

Solving KS equation:

Here, we have a chiken-egg situation. We have to solve KS equation to obtain KS orbitals that is defined in terms of E_H, E_{ext} and so on . However, those terms in turn depends on KS orbitals indirectly. Therefore, we have to follow a self-consistent method of solving KS equation:

- We choose some trial $\rho(r)$ and $E_{xc}[\rho(r)]$
- We evaluate $\hat{H}_{KS}$
- We solve KS equation and find set of orbitals $\phi_i(r)$
- We obtain new $\rho(r)$ from the newly evaluated KS orbitals
- We repeat the same process for new $\rho(r)$
- We stop when we find a set of $\phi_i(r)$ that lead us to the $\hat{H}_{KS}$ whose solutions are the same $\phi_i(r)$ we started with (we call this that the self-consistency is reached).

Exchange-correlation functional: While all other energy terms can be obtained exactly using quantum mechanics, E_{xc} must be approximated. That means the quality of E_{xc} approximation will determine the quality of the DFT.

The XC energy functional can be approximated by assuming it as a local/semilocal functional of $\rho(r)$. A spherical XC hole is also assumed. Then it takes a Hartree-like form:

$$E_{xc}[\rho(r)] = \frac{1}{2} \int \int \frac{\rho(r)\rho_{xc}^{hole}(r,r')}{|r-r'|} \, dr \, dr'$$

This express the XC energy functional as a integral over whole space of the electron density multiplied by local XC energy per electron. The local XC energy per electron is obtained as the electrostatic interaction between an electron at r and the local XC hole density at r'.

Local Density Approximation (LDA): There are many approximations for the XC energy. LDA assumes that instead of the varying electron density, there are several pieces of uniform density with different values. For example, if the whole system is assumed as a uniform gas system, the exchange energy is given as:

$$\varepsilon_x^{hom}(\rho) = C\rho^{1/3}(r)$$

However, an analytic form for the correlation energy is difficult to achieve even for this highly simplified system.

Since both exchange energy and correlation energy are functionals of electron,

$$E_{xc}^{LDA}[\rho(r)] = E_x^{LDA}[\rho(r)] + E_c^{LDA}[\rho(r)]$$

$$\Rightarrow E_{xc}^{LDA}[\rho(r)] = \int \rho(r) \left\{ \varepsilon_x^{hom}[\rho(r)] + \varepsilon_c^{hom}[\rho(r)] \right\} \, dr$$

LDA typically overestimates E_x but underestimate E_c, so there is a cancellation of errors. It underestimates lattice parameters and band gaps (50% smaller or even no gap). Also, it doesn't work for transition metals and their oxides (strongly correlated systems).

Generalized gradient approximation (GGA): While LDA is a local approximation for XC energy, GGA incorporates both local and semilocal information, i.e., it incorporates the electron density as well as its gradient at that point.

$$E_{xc}^{GGA}[\rho(r)] = \int \rho(r)\, \varepsilon_{xc}^{GGA}[\rho(r), \nabla\rho(r)]\, dr$$

Since there is no simple functional form like in LDA, the general form of GGA is expressed as LDA with an additional multiplicative factor $F(s)$:

$$E_{xc}^{GGA}[\rho(r)] = \int \rho(r)\, \varepsilon_{xc}^{LDA}[\rho(r)]\, F(s)\, dr$$

where

$$s = C\frac{|\nabla\rho(r)|}{\rho^{4/3}(r)}$$

The value of s in solids ranges from 0 to 3 and the value of $F(s)$ for various GGA is varies between $1.0 - 1.6$.

Remarks:

PW91 and *PBE* are two very popular GGA choices. At the cost of computational power, there can be better XC functional such as *meta-GGA* incorporating higher order density gradient or hybrid XC functionals.

In last two chapters, the following approximations have been used:

- Born−Oppenheimer approximation (treating the nuclear contribution separately)
- Nonrelativity approximation (particles moving in speed $v << c$)
- Mean-field approximation (Hartree approximation)
- One-electron DFT approximation (KS scheme)
- Single Slater determinant approximation for wave functions
- XC energy approximation

In next chapter, we will incorporate a few more approximations such as supercell, periodic boundary condition, pseudopotential, k-points sampling etc.