§7. DFT approach.

7.1 Kohn-Sham-Hohenberg approach (DFT theory)

We start consideration from Hartree-Fock (HF) method and formula for total energy calculation in ground state :

Kinetic energy of an electrons $E = -\frac{\hbar^2}{2m} \sum_{i=1}^N \int \varphi_i^*(r) \Delta_r \varphi_i^*(r) dr^3 + \sum_{i=1}^N \int \varphi_i^*(r) \hat{V}_{eN}(r) \varphi_i(r) dr^3 + \frac{e^2}{2} \sum_{(i \neq j)=1}^N \int |\varphi_i^*(r)|^2 \frac{1}{r_{12}} |\varphi_j(r')|^2 dr^3 dr'^3 + E_x$ (1)

The Coulomb part of the total energy is sometimes called the Hartree energy E_{H} . The exact many-particle wave function $\Psi(r_1, r_2, ..., r_N)$ must be represented by one-electron functions in combination with the Slater determinant (to satisfy Pauli exclusion principle). The one-electron functions can be found from corresponding equation:

relationship between equations

$$\left(-\frac{\hbar^2}{2m}\Delta\varphi_i(r) + V_{eN} + V_H\right)\varphi_i(r) + \int V_x(r,r')\varphi_i(r')r'^3 = \epsilon_i\varphi_i(r) \quad ,$$
(2)

here

$$V_{x}(r,r') = -\sum_{j} \frac{\varphi_{j}^{*}(r')\varphi_{j}(r)}{|r-r'|}$$
(3)

This is the so-called non-local exchange potential. "Non-locality" is due to the fact that this potential depends on the position of a given electron relative to the position of all the others. Hartree potential can be found from classical Poisson equation :

$$\Delta V_{H} = -n(r) \tag{4}$$

And the electron density is calculating by this way

$$n(r) = \sum_{i=1}^{N} \left| \varphi_i(r)^2 \right| \tag{5}$$

The HF method gives a ready to use scheme to calculate any physical properties of many-particle systems such as molecules, atoms, solids . It is important to emphasize that this method ignores one multi particle effect. Representing an exact many-particle function as a combination of one-electron functions leads to the loss of many-particle correlation effects in a physical system. To correct this situation, it is necessary to include an additional correlation potential energy to the corresponding Schrodinger equation V_c .

While this approach is useful, it has some important drawbacks. To calculate the energy in the ground state, one has to operate with a large number of individual particles and, accordingly, coordinates and wave functions. Calculations require large computer resources and can only be performed on supercomputers, even for a simple systems. The breakthrough came after the presentation of the Kohn-Sham-Hohenberg(KSH) or Density Functional theory(DFT). The DFT can be called by exactification, development and simplification of HF theory.

Theorem 1. The external potential (and hence the total energy), is a unique functional of the electron density. If two systems of electrons, one trapped in a potential $V_1(r)$ the other in $V_2(r)$, have the same ground-state density n(r), then $V_1(r)-V_2(r)$ is necessarily a constant.

Corollary 1: The ground-state density uniquely determines the potential and thus all properties of the system, including the many-body wavefunction. In particular, the KSH functional, defined as, is a universal functional of the density (not depending explicitly on the external potential).

Corollary 2: In light of the fact that the sum of the occupied energies provides the energy content of the Hamiltonian, a unique functional of the ground state charge density, the spectrum of the Hamiltonian is also a unique functional of the ground state charge density.

Theorem 2.The functional that delivers the ground-state energy of the system gives the lowest energy if and only if the input density is the true ground-state density. In other words, the energy content of the Hamiltonian reaches its absolute minimum, i.e., the ground state, when the charge density is that of the ground state. For any positive integer and potential, a density functional exists such that reaches its minimal value at the ground-state density of electrons in the potential. The minimal value of is then the ground-state energy of this system.

It means that for ground state the total energy of system can be calculated by using only electron density function defined in all points of space (5). Knowledge of this function allow to recover the multi-particle wave function and potential energy function for nuclei and viceversa. The DFT approach is strongly simplify the calculations for ground state of crystals because instead of large system of wave functions defined at all points of space we need to use only one function (electron density n(r)). But what does the density functional of energy look like? Lets start from (1):

$$E = -\frac{\hbar^{2}}{2m} \sum_{i=1}^{N} \int \varphi_{i}^{*}(r) \Delta_{r} \varphi_{i}^{*}(r) dr^{3} + \sum_{i=1}^{N} \int \varphi_{i}^{*}(r) \hat{V}_{eN}(r) \varphi_{i}(r) dr^{3} + \frac{e^{2}}{2} \sum_{(i \neq j)=1}^{N} \int |\varphi_{i}^{*}(r)|^{2} \frac{1}{r_{12}} |\varphi_{j}(r')|^{2} dr^{3} dr'^{3} + E_{xc}$$

$$I \qquad II \qquad III \qquad III \qquad III \qquad IV$$
(6)

First of all in framework of DFT the exchange and correlation energies should be combined into exchangecorrelation (EX) energy (potential) $E_x + E_c = E_{xc}$ and for corresponding operators $\hat{V}_{xc} = \hat{V}_c + \hat{V}_x$. We will talk about EX later.

The expression for kinetic energy (I) through electron density function can be taken from theory for free electrons where kinetic energy is proportional to $E_{kin} \sim n^{\frac{5}{3}}$.

In second (II) and third (III) terms the wave functions and sums can be directly combines to density function (5).

After combination we have:

$$E(n) = C_{kin} n^{\frac{5}{3}}(r) + \int n(r) \hat{V}_{eN}(r) dr^{3} + e^{2} \int \frac{n(r)n(r')}{r_{12}} dr^{3} dr'^{3} + E_{xc}$$
(7)

Most complicated part related to E_{xc} energies. We start from exchange E_x contribution. The exchange energy in HF approximation is looks like this:

$$E_{x} = -\frac{e^{2}}{2} \sum_{(i\neq j)=1}^{N} \int \varphi_{i}^{*}(r) \varphi_{i}(r') \frac{1}{r_{12}} \varphi_{j}(r) \varphi_{j}^{*}(r') dr^{3} dr'^{3}$$
(8)

This equation can be represented in DFT representation by using model of free electrons. The wave function for free electron in 3D space is looks like so:

$$\varphi_k(r) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \tag{9}$$

In (8) in this case instead of quantum numbers **i** and **j** we have to use the wave vectors **k** and **k'**. After substitution (9) to (8) and change summation by integration by using relation:

$$\sum_{i} \Rightarrow \sum_{\vec{k}} \Rightarrow \frac{V}{(2\pi)^{3}} \int_{\text{over } k \le k_{F}} d^{3}k$$
(10)

we have:

$$E_{x} = \frac{1}{(2\pi)^{6}} \int_{\text{over } k \le k_{F}} dk^{3} \int_{\text{over } k \le k_{F}} dk'^{3} \int_{\text{over } V} dr^{3} \int_{\text{over } V} dr'^{3} \frac{e^{-i(k-k')(r-r')}}{|r-r'|}$$
(11)

For zero temperature, the first two integrals should be calculated for points located in k-space inside a sphere with radius k_F (Fermi radius), and the second two integrals should be calculated for the entire volume of the crystal.

Using new variables $u = k_F(r - r')$ and $q = \frac{k}{k_F}$, $q' = \frac{k'}{k_F}$ for E_x we have:

$$E_{x} = \frac{C k_{F}^{4} V}{(2 \pi)^{6}}, \quad \text{here } C = \int_{q \le 1} dq^{3} \int_{q' \le 1} dq'^{3} \frac{e^{-i(q-q')u}}{|u|} = \frac{16}{\pi^{3}}$$
(12)

It is clear that for exchange energy we have the next dependence on density function $E_x \sim n^{\frac{4}{3}}$. Estimation for correlation part of total energy was done through Monte-Carlo simulations. There is the next approximated formula for correlation energy E_c :

$$E_{c} = n \cdot V \cdot \begin{pmatrix} 0.0311 \ln r_{s} - 0.048 - 0.002 r_{s} \ln r_{s} - 0.0116 r_{s}, \text{ if } r < r_{s} \\ - \frac{0.1423}{1 + 1.0529 \sqrt{r_{s}} + 0.3334 r_{s}}, \text{ if } r \ge r_{s} \end{pmatrix}$$
(13)

Of course it is not the only one possible option for representation of correlation part. Here r_s is a radius of sphere occupied by one electron. The corresponding radius can be calculated from next equation:

$$\frac{4\pi}{3}r_{s}^{3} = \frac{V}{N} = \frac{1}{n}$$
(14)

In the framework of DFT the self consistent calculation cycle is looks like so (step by step):

1. At the beginning we must first define the one-electron wave functions. This can be done in many ways. Most simplest is present wave functions as a Fourier series:

$$\varphi(r) = \sum_{\vec{k}} C_k e^{i\vec{k}\vec{r}}$$
(15)

We need to define some constraint on the values of the wave vector. This can be done by imposing the following constraint on the kinetic energy of electrons in the free electron approximation:

$$\frac{\hbar^2 k^2}{2m} \le E_{cut} \tag{16}$$

2. Now the density of electrons can be calculated by using (5).

3. Here can be defined exchange-correlation part of total potential and Hartree part can be found from corresponding Poisson equation (4).

4. Now should be created total potential in form:

$$V_{tot} = V_{eN} + V_H + V_{XC} \tag{17}$$

5. New we need to solve Kohn-Hohenberg equation to calculate new one electron wavefunctions and new density function:

$$\left(-\frac{\hbar^2}{2m}\Delta + V_{tot}\right)\varphi_i(r) = \epsilon_i \varphi_i(r)$$
(18)

6. If difference between new total energy (7) and total energy from previous SC cycle is less than some E_{diff} :

$$\left|E_{new} - E_{previous}\right| \le E_{diff} \tag{19}$$

the calculation can be finished otherwise we go to step 3. The cycle will end after condition (19) is met.

This method is applicable to different types of simple and complex manyatomic systems. In fact, most of the physical properties, such as: structure optimization, elastic constants, phonon spectrum and related properties, optical and magnetic properties, etc. can be numerically calculated.

Some additional simplification can be made by using only valence (outer) electrons in the calculations. But this simplification requires the inclusion of internal electrons in the nucleus of an atom and the generation for this complex, the nucleus plus internal electrons, of the so-called pseudopotential.

The correct generation of pseudopotential is a separate and complicated task but for most ab-initio packages it successfully already done.