The following note is based on the Coursera Mooc ***Density Functional Theory*** by ***École Polytechnique*** which is available at https://www.coursera.org/learn/density-functional-theory

Week 2: From density to Kohn-Sham world

Auxiliary system:

We now turn to auxiliary system approach where we imagine a system very close enough to the original system but tractable. And then we try to relate this auxiliary system to the original system and see if we can extract any information about the original system by investigating the auxiliary system. So, we ask: ***what is a good auxiliary system for many-body problem?***

So, instead of the interacting many-body Schrödinger equation, we imagine a non-interacting auxiliary system, for which the equation is (in atomic units):

$$\left(-\frac{\nabla^2}{2}+U_{aux}(r)\right)\phi_l^{aux}(r)=\varepsilon_l^{aux}\phi_l^{aux}(r)$$

Here, the $U_{aux}(r)$ is the non-interacting potential for the auxiliary system. Notice that the solutions(orbitals) and eigenvalues are not the solutions/eigenvalues of the original system. These are eignevalues/solutions of the oxiliary system.

We now hope that such oxiliary potential exists.

Kohn-Sham (KS) System:

KS system is a type of auxiliary system. In KS system we assume a noninteracting electron system (we will compensate for the interaction). Here, by using the old ideas such as Hartree approach, we can rewrite the total energy functional as following (Let T be the total kinetic energy and T_s be the kinetic energy for non-interacting electron system):

$$\begin{aligned}E[\rho]&=T[\rho]+\int\rho\,U_{ext}\,dr+E_{ee}[\rho]\\&=T[\rho]+\int\rho\,U_{ext}\,dr+E_{ee}[\rho]+T_s[\rho]-T_s[\rho]+E_H[\rho]-E_H[\rho]\\&=T_s[\rho]+\int\rho\,U_{ext}\,dr+E_H[\rho]+E_{xc}[\rho]\end{aligned}$$

where $E_{xc}[\rho]=T[\rho]-T_s[\rho]+E_{ee}[\rho]-E_H[\rho]$.

Notice, that the total energy functional is the same as in the Hartree approach with an added exchange-correlation energy functional. So, now the problem simplifies to approximate just one term, E_{xc}.

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Kohn-Sham (KS) equation:

In the Kohn-Sham approach, the $U_{aux}(r)$ takes the following form:

$$U_{KS}(r) = U_{ext} + U_H + U_{xc}$$

Then we solve the KS equation for non-interacting electrons of the auxiliary system that give the exact electron density of the real system. The KS equation is:

$$\left(-\frac{\nabla^2}{2} + U_{KS}(r)\right)\phi_i(r) = \hat{H}_{KS}\ \phi_i(r) = \varepsilon_i\phi_i(r)$$

After solving the equation, we get the KS orbitals and consequently, the density.

$$\rho(r) = \sum_i |\phi_i(r)|^2$$

Since theoretically we can construct any observable as a functional of the density, we can get the value of any observable by solving this equation.

$$\phi_i(r) \rightarrow \rho(r) \rightarrow E[\rho(r)] \rightarrow \text{almost everything (phonons, stability, defects, ...)}$$

However, we don't know the exact form of the XC functional.

Kohn-Sham world:

We talked about the KS system and equation, but how to solve them? What is the physical significance of the solutions?

The KS equations can be solved by the self-consisent method as we did in case of Hartree approach. The initial guess for the $U_{KS}(r)$ is $U_{ext}(r)$. Then for every iteration we modify $U_{KS}(r)$ as the following:

$$U_{KS,\,new}(r) \rightarrow U_{KS,\,old}(r) + \mu\left[\rho_{KS,\,old}(r)^p - \rho_{target}(r)^p\right]$$

Here, μ and p are only for algorithmic stability and have no effect on the solution.

The eigenvalues of the KS equation has the dimension of enegy but they do **NOT** represent the real energy of the electron of the real system. The eigenvalues have very real use in material science but their physical significance is not clear (yet).