

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 1: From many-body problem to DFT**

The many-body problem: We start by writing the many-body Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|}$$

Here, i, j range over the number of electrons, and I, J range over the number of nuclei. Since the mass of the nuclei is much larger than of electron, we can neglect the kinetic energy term due to nuclei. Also, the Coulomb interaction term between nuclei is just a constant since there movement in a system can be ignored. So, what ultimately remains is:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

Now there might be some other potential coming outside from the system. We call all such potential in addition with the potential coming from the nuclei as the external potential and we write:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i U_{ext}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

However, even this simplified equation is impossible to tackle exactly.

Observables and Functional:

What we want from a system are the observables. In QM, they are the expectation value. Let O be an observable. Then, in μVT ensemble:

$$O = \langle \hat{O} \rangle = \frac{1}{Z} \sum \alpha e^{-\beta(E_\alpha - \mu N_\alpha)} \langle \psi_\alpha | \hat{O} | \psi_\alpha \rangle$$

That means the observable can be expressed as a functional of the wavefunction. However, the wavefunction is too complicated to calculate. That's why one way to approach is to approximate the wavefunction. Some of the such approaches are: Hartree-Fock, Quantum Monte Carlo etc.

However, we could rewrite the functional in terms of completely something else such as instead of ψ , we can use U_{ext} . So, instead of $O[\psi]$, a functional of wavefunction, we are looking for

$\tilde{O}[U_{ext}]$, a functional of the external potential. But now, the functional would be too difficult to evaluate.

$$\begin{aligned} O[\psi] &: \text{Simple functional of complicated function} \\ \tilde{O}[U_{ext}] &: \text{Complicated functional of simple function} \end{aligned}$$

That's why we are looking for another functional. In this course, we will see that the functional will be of electron density, $\rho(r)$, i.e., we are looking for:

$$O[\rho(r)] : \text{The goal}$$

Also, we want different functionals of this same function for all observables that would make our life easier. Observables can include but not limited to equilibrium bond angle & length, ground state properties, etc.

We skip the *functional derivative* part.

Hohenberg-Kohn (HK) theorem: We know the statements of two HK theorems from the lecture note of **Lee (Chapter 5)**. Let us give here a proof scheme for the first theorem.

Let two external potential differ by more than a constant, i.e., $U_{ext}^{(1)} \neq U_{ext}^{(2)} + \text{const.}$ and they gave rise to same ground state density. Therefore,

$$\begin{aligned} H_1 |\psi_g\rangle &= E_1 |\psi_g\rangle \\ H_2 |\psi_g\rangle &= E_2 |\psi_g\rangle \\ \Rightarrow [U_{ext}^{(1)} - U_{ext}^{(2)}] |\psi_g\rangle &= (E_1 - E_2) |\psi_g\rangle \\ \Rightarrow U_{ext}^{(1)} &= U_{ext}^{(2)} + \text{const.} \end{aligned}$$

which violates our assumption. Therefore, there cannot be two different external potential leading to the same ground state electron density.

An important remark: HK theorem only establishes the uniqueness of the external potential and the electron density. It says nothing about the existence of such functional.