

Density Functional Theory in a Nutshell

Introduction

The goal of Density Functional Theory (DFT) is to solve ground states of many-body systems, mainly focused on electronic systems. Suppose we got N electrons flying around in an external potential field. When simulating the realistic materials (e.g., crystals or molecules), this potential is usually taken as the Coulomb interaction between electrons and nucleus. Thus, the Hamiltonian of the system is of the form

$$H = T + U_{ee} + U_{\text{ext}}, \quad (1)$$

where T is the kinetic energy term of the electrons, U_{ee} is the interaction between electrons, and U_{ext} is the external potential field where these electrons live. What needs to be pointed out is that the first two terms $\tilde{H} = T + U_{ee}$ is universal for all N -electron systems, i.e., \tilde{H} has exactly the same form for all N -electron problems.

Density

The state of this system is described by the wave-function

$$|\Psi\rangle = \Psi(x_1, x_2, \dots, x_N), \quad (2)$$

where x_k is the spatial coordinate of the k -th particle.¹ This wave function has permutation symmetry.

$$\Psi(x_1, \dots, x_k, \dots, x_N) = -\Psi(x_k, \dots, x_1, \dots, x_N), \text{ for } k > 1. \quad (3)$$

The number density $n(x)$, by definition, is the expectation of particle number at a specific position x . Thus, we have

$$\begin{aligned} n(x) &= \langle \Psi | \sum_{k=1}^N \delta(x_k - x) | \Psi \rangle \\ &= \int dx_1 \cdots dx_N \sum_{k=1}^N \delta(x_k - x) |\Psi(x_1, \dots, x_N)|^2 \\ (\text{the integral of } \delta\text{-function is trivial}) &= \sum_{k=1}^N \int dx_1 \cdots dx_N \int dx_k \delta(x_k - x) |\Psi(x_1, \dots, x_k, \dots, x_N)|^2 \\ (|\Psi|^2 \text{ does not change under permutation}) &= \sum_{k=1}^N \int dx_1 \cdots dx_N |\Psi(x, \dots, x_1, \dots, x_N)|^2 \\ &= N \int dx_2 \cdots dx_N |\Psi(x, x_2, \dots, x_N)|^2. \end{aligned} \quad (4)$$

External Potential

Suppose the given potential is $v(x)$, then the external potential energy is, can be computed in a similar way of the definition of the density function²,

$$\langle \Psi | U_{\text{ext}} | \Psi \rangle = \langle \Psi | \sum_{k=1}^N v(x_k) | \Psi \rangle = \int dx v(x) n(x). \quad (5)$$

Thus, the external energy term is a functional of the density,

¹Technically, electrons are identical particle. So actually, we cannot label them.

²See Appendix for detailed computation.

$$U_{\text{ext}} = U_{\text{ext}}[n]. \quad (6)$$

Hohenberg-Kohn Theorem

[ToAdd: a more concrete and more mathematical description of the correspondence.]

Suppose $|\Psi\rangle$ is the ground state of Hamiltonian

$$H = \tilde{H} + \sum_{k=1}^N v(x_k), \quad (7)$$

and $|\Psi'\rangle$ is the ground state of Hamiltonian

$$H = \tilde{H} + \sum_{k=1}^N v'(x_k). \quad (8)$$

By the definition of ground state³, we have,

$$\begin{aligned} \langle \Psi' | H | \Psi' \rangle &\geq \langle \Psi | H | \Psi \rangle \\ \Rightarrow \langle \Psi' | \tilde{H} | \Psi' \rangle + \int dx v(x) n'(x) &\geq \langle \Psi | \tilde{H} | \Psi \rangle + \int dx v(x) n(x). \end{aligned} \quad (9)$$

If the two states, $|\Psi\rangle$ and $|\Psi'\rangle$, gives the same density, i.e., $n(x) = n'(x)$. Then we would have

$$\langle \Psi' | \tilde{H} | \Psi' \rangle \geq \langle \Psi | \tilde{H} | \Psi \rangle. \quad (10)$$

Similarly for H' , we have

$$\begin{aligned} \langle \Psi | H' | \Psi \rangle &\geq \langle \Psi' | H' | \Psi' \rangle \\ \Rightarrow \langle \Psi | \tilde{H} | \Psi \rangle + \int dx v'(x) n(x) &\geq \langle \Psi' | \tilde{H} | \Psi' \rangle + \int dx v'(x) n'(x) \\ \Rightarrow \langle \Psi | \tilde{H} | \Psi \rangle &\geq \langle \Psi' | \tilde{H} | \Psi' \rangle. \end{aligned} \quad (11)$$

Again, the derivation in the last step is based on the assumption $n(x) = n'(x)$.

Combine this two inequalities, we know that if two (ground) states lead to the same density, then they lead to the same universal energy term expectation. In other words, the value of universal term **can** be determined by the density. Thus, it is a functional of the density

$$\tilde{H} = \tilde{H}[n]. \quad (12)$$

Non-Interacting Electronic Gas

Discussing the non-interacting model here seems a little bit weird. But this is actually the preparation for the next part. For non-interacting electrons, their Hamiltonian is of the form

$$H_{\text{non}} = T + U_{\text{ext}}. \quad (13)$$

So solving this system is minimizing the functional⁴

$$E[n] = T[n] + \int dx v(x) n(x), \quad (14)$$

which gives a variational equation

³Energy expectation of all other states is no less than the ground state energy

⁴Whether the kinetic energy T can be written as a functional of the density $n(x)$ remains unproven.

$$\frac{\delta T}{\delta n} + v(x) = 0. \quad (15)$$

In another point of view, since there is no interaction between the electrons, we are actually solving N **independent** single-body Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + v(x)\right)\phi_k(x) = \varepsilon_k \phi_k(x). \quad (16)$$

And the density is given by

$$n(x) = \sum_k f_k |\phi_k(x)|^2, \quad (17)$$

where f_k is the occupation number of orbital k . Although this expression seems a little different from Eq. 4, they are the same. It actually serves as a good practice for the reader to check that this two expression leads to the same result for non-interacting electrons. (*Hint: wave-functions of different orbitals are orthogonal.*)

Kohn-Sham Equation

From the Hohenberg-Kohn theorem, a general form of the energy functional is⁵

$$E[n] = T[n] + U_{ee}[n] + U_{\text{ext}}[n], \quad (18)$$

and minimizing this functional gives a variational equation

$$\frac{\delta T}{\delta n} + \frac{\delta U_{ee}}{\delta n} + v(x) = 0. \quad (19)$$

Compare Eq. 19 with Eq. 15, and we can find out that they are of the same form

$$\frac{\delta T}{\delta n} + v_{\text{eff}}(x) = 0, \quad (20)$$

with the definition

$$v_{\text{eff}}(x) = v(x) + \frac{\delta U_{ee}}{\delta n}. \quad (21)$$

Thus, we can introduce a **non-interacting** model living in the effective potential $v_{\text{eff}}(x)$. And the ground state of this model is exactly the ground state of the original interacting system. Because they are solutions of the same variational equation.

Coulomb Interaction: An Example

The Coulomb energy of the system can be written as

$$U_{\text{lr}} = \frac{1}{2} \int dx dx' \frac{n(x)n(x')}{|x - x'|}, \quad (22)$$

where the one-half factor is due to the double counting. Now suppose we got two density $n(x)$ and $\tilde{n}(x) = n(x) + \eta(x)$, the differential is

⁵Again, whether the kinetic energy T and interaction U_{ee} can be separately written as functional of density n remains unproven.

$$\begin{aligned}
U_{\text{lr}}[\tilde{n}] - U_{\text{lr}}[n] &= \frac{1}{2} \int dx dx' \frac{\tilde{n}(x)\tilde{n}(x') - n(x)n(x')}{|x - x'|} \\
&= \frac{1}{2} \int dx dx' \frac{n(x)\eta(x') + n(x')\eta(x) + O(\eta^2)}{|x - x'|} \\
&= \int dx dx' \frac{n(x')\eta(x)}{|x - x'|} + O(\eta^2) \\
&= \int dx \eta(x) \int dx' \frac{n(x')}{|x - x'|} + O(\eta^2).
\end{aligned} \tag{23}$$

Thus, the variational is

$$\frac{\delta U_{\text{lr}}}{\delta n} = v_{\text{lr}}(x) = \int dx' \frac{n(x')}{|x - x'|}. \tag{24}$$

Besides the long-range Coulomb interaction, there are also other interactions between electrons, such as exchange terms and correlation terms (denoted as U_{xc}).

Solving the Kohn-Sham Equation

The Kohn-Sham equation can be solved through a self-consistent loop: First, insert a trial density $n_{\text{trial}}(x)$ into the effective potential $v_{\text{eff}}(x)$. Then solve the eigen-states $\{\phi_k(x)\}$ of the Kohn-Sham equation. Finally, update the density from the solution $\{\phi_k(x)\}$ and go over this process again.

This process can be described by the following flow chart.

