

Lecture on First-principles Computation (5): General Introduction to Density Functional Theory

任新国 (Xinguo Ren)

中国科学技术大学
量子信息重点实验室

Key Laboratory of Quantum Information, USTC

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Basic idea behind density functional theory

The many-body Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} = \sum_i^N -\frac{\nabla_i^2}{2m} + \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N V_{ext}(\mathbf{r}_i)$$

The ground-state energy:

$$E_0[\Psi] = \langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V}_{ee} | \Psi \rangle + \langle \Psi | \hat{V}_{ext} | \Psi \rangle$$

The ground-state density

$$n = \langle \Psi | \hat{n} | \Psi \rangle = \langle \Psi | \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle$$

$$E_0 = E_0[\Psi] \xrightarrow{\text{?}} E_0 = E_0[n]$$

If one can avoid complex many-body wave function, and **express the ground-state energy as a function of the electron density**, then the problem will be significantly simplified.

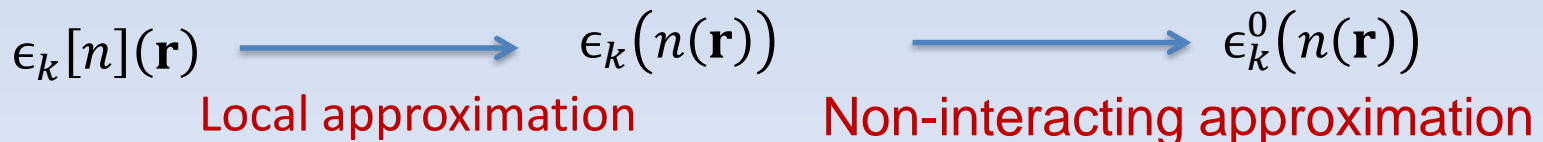
Early-day DFT: Thomas-Fermi approximation

$$E[\Psi] = \langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V}_{ee} | \Psi \rangle + \langle \Psi | \hat{V}_{ext} | \Psi \rangle$$

Kinetic energy: $T = \langle \Psi | \hat{T} | \Psi \rangle = \int d^3 r n(\mathbf{r}) \epsilon_k[n](\mathbf{r}) \approx \int d^3 r n(\mathbf{r}) \epsilon_k^0(n(\mathbf{r}))$

$\epsilon_k[n](\mathbf{r})$: The kinetic energy density at point \mathbf{r} , which depends on the electron density in the whole space, is a functional of the electron density n

$\epsilon_k^0(n(\mathbf{r}))$: The kinetic energy density of non-interacting HES, which only depends on the electron density at \mathbf{r} : $n(\mathbf{r})$



The Thomas-Fermi approximation (1927,1928)

$$E[\Psi] = \langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V}_{ee} | \Psi \rangle + \langle \Psi | \hat{V}_{ext} | \Psi \rangle$$

Electron-electron and electron-nuclear interaction energy:

$$V_{ee} = \langle \Psi | \hat{V}_{ee} | \Psi \rangle = E_{\text{Hartree}}[n(\mathbf{r})] + U_{\text{XC}}[n(\mathbf{r})]$$

$$E_{ext} = \langle \Psi | \hat{V}_{ext} | \Psi \rangle = \int d^3 r n(\mathbf{r}) v_{ext}(\mathbf{r})$$

In summary:

$$E_{\text{TF}}[n(\mathbf{r})] = \int d^3 r n(\mathbf{r}) \epsilon_k^0(n(\mathbf{r})) + \frac{1}{2} \int d^3 r d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 r n(\mathbf{r}) v_{ext}(\mathbf{r})$$

The Thomas-Fermi equation

Under the Thomas-Fermi approximation, the ground-state energy of an electronic system is an **explicit functional of the electron density!**

$$\epsilon_k^0(n) = \frac{3}{5} \epsilon_F(n) = \frac{3}{10m} (3\pi)^{2/3} n^{2/3} = C_k n^{2/3}, \quad C_k = \frac{3}{10m} (3\pi)^{2/3}$$

$$E_{\text{TF}}[n(\mathbf{r})] = C_k \int d^3 r n^{5/3}(\mathbf{r}) + \frac{1}{2} \int d^3 r d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 r n(\mathbf{r}) v_{\text{ext}}(\mathbf{r})$$

Minimizing the ground-state energy with respect to the electron density, under the constraint

$$\int d^3 r n(\mathbf{r}) = N$$

$$\delta \left\{ E_{\text{TF}}[n(\mathbf{r})] - \mu \left(\int d^3 r n(\mathbf{r}) - N \right) \right\} = 0$$

The Thomas-Fermi equation

$$E_{\text{TF}}[n(\mathbf{r})] = C_k \int d^3 r n^{5/3}(\mathbf{r}) + \frac{1}{2} \int d^3 r d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 r n(\mathbf{r})v_{\text{ext}}(\mathbf{r})$$

$$\delta \left\{ E_{\text{TF}}[n(\mathbf{r})] - \mu \left(\int d^3 r n(\mathbf{r}) - N \right) \right\} = 0$$



$$\left\{ \begin{array}{l} 5/3 C_k n^{2/3}(\mathbf{r}) + v_{\text{eff}}(\mathbf{r}) - \mu = 0 \\ v_{\text{eff}}(\mathbf{r}) = \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{ext}}(\mathbf{r}) \end{array} \right.$$

$$V_{\text{Hartree}}(\mathbf{r})$$

Solving this equation, one obtains the ground-state electron density and the ground-state energy.

Dirac's exchange correction (1930)

Further accounting for the exchange contribution:

$$E_{\text{TFD}}[n(\mathbf{r})] = E_{\text{TF}}[n(\mathbf{r})] + E_x^0[n(\mathbf{r})]$$

The exact exchange energy of an inhomogeneous system cannot be expressed as an explicit functional of the electron, and **here we again adopt the local approximation**.

$$E_x^0[n(\mathbf{r})] = \int d^3 r n(\mathbf{r}) \epsilon_x^0(n(\mathbf{r})) = C_x \int d^3 r n^{4/3}(\mathbf{r})$$

$$C_x = -3/4 \left(\frac{3}{\pi} \right)^{1/3} \approx -0.739$$

$$\delta \left\{ E_{\text{TFD}}[n(\mathbf{r})] - \mu \left(\int d^3 r n(\mathbf{r}) - N \right) \right\} = 0$$

$$5/3 C_k n^{2/3}(\mathbf{r}) + v_{\text{eff}}(\mathbf{r}) - \mu = 0$$

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{Hartree}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) + v_x(\mathbf{r})$$

$$-(3/\pi)^{1/3} n^{1/3}(\mathbf{r})$$



Deficiencies of the Thomas-Fermi approximation

- The charge density at the nuclear position is infinite
- The charge density away from the nucleus shows a $1/r^6$ decay, instead of the correct exponential decay.
- Atoms have no shell structure, and hence the periodic table of elements cannot be obtained.
- Atoms cannot bind and form molecules and solids.

Slater's $X\alpha$ method (1951)

- Hartree-Fock-Slater equation:

(Initially as an approximation to the Hartree-Fock equation)

$$\left(-\frac{\nabla^2}{2m} + v_{ext}(\mathbf{r}) + v_{Hartree}(\mathbf{r}) + v_{X\alpha}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r})$$

$$v_X \phi_l(\mathbf{r}) = \int d\mathbf{r}' v_X(\mathbf{r}, \mathbf{r}') \phi_l(\mathbf{r}') \approx v_{X\alpha}(\mathbf{r}) \phi_l(\mathbf{r})$$

$$v_{X\alpha}(\mathbf{r}) = -\alpha \frac{3}{2} \left(\frac{3}{\pi} \right)^{1/3} n^{1/3}(\mathbf{r})$$



John C. Slater

$\alpha=1 \rightarrow$ Slater local exchange

$\alpha=2/3 \rightarrow$ Kohn-Sham local exchange

Slater's $X\alpha$ method (1951)

- Hartree-Fock-Slater equation:

$$\left(-\frac{\nabla^2}{2m} + v_{ext}(\mathbf{r}) + v_{Hartree}(\mathbf{r}) + v_{X\alpha}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r})$$

$$v_{X\alpha}(\mathbf{r}) = -\alpha \frac{3}{2} \left(\frac{3}{\pi} \right)^{1/3} n^{1/3}(\mathbf{r})$$

Slater $X\alpha$ ($\alpha=2/3$) method: the ground-state energy

$$E_{\text{HFS}} = \sum_{i=1}^N \langle \phi_i | -\frac{\nabla^2}{2m} | \phi_i \rangle + E_{Hartree}[n] + E_{ext}[n] + E_x^0[n]$$

Apart from the kinetic energy, the total energy form of Slater $X\alpha$ ($\alpha=2/3$) is the same as the Thomas-Fermi-Dirac method.

Slater's $X\alpha$ method (1950's-1970's)

Slater $X\alpha$ ($2/3 \leq \alpha \leq 1$ as an adjustable parameter) method has been widely used for computations of atoms, molecules, and solids, and was the major method for calculating realistic systems during 1950's – 1970's. Historically Slater's $X\alpha$ method was viewed as an approximation to the Hartree-Fock method. But in hindsight, Slater $X\alpha$ can be better seen as an approximate density functional theory.

Kohn's thought on the Thomas-Fermi theory

Now a very crude theory of electronic energy in terms of the electron density distribution, $n(\mathbf{r})$, the Thomas-Fermi (TF) theory, has existed since the 1920s. It was quite useful for describing some qualitative trends, e.g., for the total energy of atoms, but for questions of chemistry and materials science, which involve valence electrons, it was of almost no use; for example it did not lead to any chemical binding. However the theory has one feature which interested me: It considered interacting electrons moving in an external potential $v(\mathbf{r})$, and provided a highly over-simplified one-to-one implicit relation between $v(\mathbf{r})$ and the density distribution $n(\mathbf{r})$.

-- *Walter Kohn, Nobel lecture, 1999*

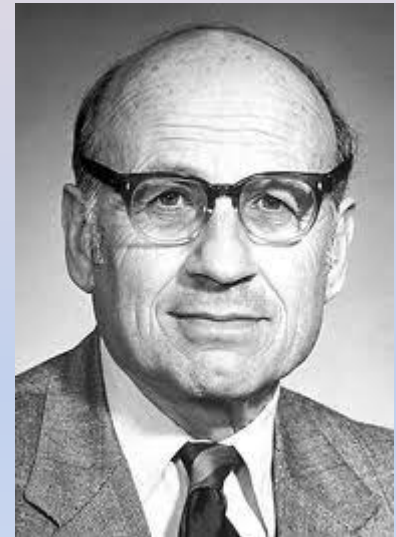
Kohn's thought on Thomas-Fermi (TF) theory

$$\frac{5}{3}n^{2/3}(\mathbf{r}) + V_{eff}(\mathbf{r}) - \mu = 0, \quad C_k = \frac{3}{10m}(3\pi)^{2/3}$$

$$\mu - V_{eff}(\mathbf{r}) = \frac{1}{2m} [3\pi n(\mathbf{r})]^{2/3}$$

$$V_{ext}(\mathbf{r}) = V_{eff}(\mathbf{r}) - \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Therefore, in Thomas-Fermi theory, the external potential is uniquely determined by the electron density (up to a constant μ). Furthermore, because $N = \int d^3 r' n(\mathbf{r}')$, thus for a given ground-state electron density, the Hamiltonian of the electronic system is completely determined.



Walter Kohn

Kohn's thought on Thomas-Fermi (TF) theory

This raised a general question in my mind: Is a *complete, exact* description of ground-state electronic structure in terms of $n(\mathbf{r})$ possible in principle? A key question was whether the density $n(\mathbf{r})$ completely characterized the system.

---- Walter Kohn, before 1963

Hohenberg-Kohn theorem I

$$\hat{H} = - \sum_i^N \frac{\nabla_i^2}{2m} + \frac{1}{2} \sum_{i \neq j}^N V(\mathbf{r}_i, \mathbf{r}_j) + \sum_i^N v_{ext}(\mathbf{r}_i)$$

Theorem I:

For any system of interacting particles in an external potential $v_{ext}(\mathbf{r})$, the potential is determined uniquely, except for a constant, by the ground-state particle density $n_0(\mathbf{r})$.

P. Hohenberg & W. Kohn, (1964)

Phys. Rev. **136**, B864 (1964).

Proof of the Hohenberg-Kohn Theorem I

“Reductio ad absurdum” (reduction to absurd, 归谬法)

Assume there exists two external potentials $v_{ext}^A(\mathbf{r})$, $v_{ext}^B(\mathbf{r})$, which differ by more than a constant, but yield the same ground-state electron density $n_0(\mathbf{r})$,

$$E^A = \langle \Psi_A | \hat{H}^A | \Psi_A \rangle < \langle \Psi_B | \hat{H}^A | \Psi_B \rangle$$

Non-degenerate
ground state

$$\langle \Psi_B | \hat{H}^A | \Psi_B \rangle = E^B + \int d^3 n(\mathbf{r}) (v_{ext}^A(\mathbf{r}) - v_{ext}^B(\mathbf{r}))$$



$$E^A < E^B + \int d^3 n(\mathbf{r}) (v_{ext}^A(\mathbf{r}) - v_{ext}^B(\mathbf{r}))$$

$$E^B < E^A + \int d^3 n(\mathbf{r}) (v_{ext}^B(\mathbf{r}) - v_{ext}^A(\mathbf{r}))$$

Summing up the two equations

$$E^A + E^B < E^A + E^B$$

This is not possible, and the original assumption is wrong.

Corollary of the Hohenberg-Kohn theorem I

The Hamiltonian of an interacting electron systems is fully determined by its ground-state density, apart from a constant. Therefore, both the ground state and excited states, and hence all properties of the system are completely determined by its ground-state density.

Hohenberg-Kohn (HK) theorem II

A **universal functional** for the energy E in terms of the density $n(\mathbf{r})$, $F[n]$, can be defined, valid for any external potential $v_{ext}(\mathbf{r})$. The exact ground-state energy E_0 of the system is the global minimum value of the functional,

$$E_v[n] = F[n] + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r})$$

and the density $n(\mathbf{r})$ that minimizes the functional $E_v[n]$ is the exact ground state density $n_0(\mathbf{r})$.

Proof of Hohenberg-Kohn Theorem II

Assume $n(\mathbf{r})$ is a “V-representable” particle density, i.e., $n(\mathbf{r})$ is a ground-state particle density associated with a physically realizable external potential $v_{ext}(\mathbf{r})$.

$$\begin{aligned} E_{\text{HK}}[n] &= \langle \Psi_0[n] | \hat{H} | \Psi_0[n] \rangle \\ &= \langle \Psi_0[n] | \hat{T} + \hat{V}_{ee} | \Psi_0[n] \rangle + \int d^3 r v_{ext}(\mathbf{r}) n(\mathbf{r}) \\ &= F_{\text{HK}}[n] + \int d^3 r v_{ext}(\mathbf{r}) n(\mathbf{r}) \end{aligned}$$

$$n(\mathbf{r}) \rightarrow \Psi_0 \rightarrow F_{\text{HK}}$$

$F_{\text{HK}}[n]$: does not depend the external potential and is hence called “*universal functional*”.

Proof of the Hohenberg-Kohn Theorem II

$$\begin{aligned} E_{\text{HK}}[n] &= \langle \Psi_0[n] | \hat{H} | \Psi_0[n] \rangle \\ &= F_{\text{HK}}[n] + \int d^3 r v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \end{aligned}$$

Assume the external potential of current system is $v_{\text{ext}}(\mathbf{r})$, and its ground-state density is $n_0(\mathbf{r})$. For any other density $n'(\mathbf{r}) \neq n_0(\mathbf{r})$ its ground-state wave function is

$$\begin{aligned} E_{\text{HK}}[n_0] &= \langle \Psi_0[n_0] | \hat{H} | \Psi_0[n_0] \rangle \\ &< \langle \Psi'[n'] | \hat{H} | \Psi'[n'] \rangle = E_{\text{HK}}[n'] \end{aligned}$$