

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

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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.

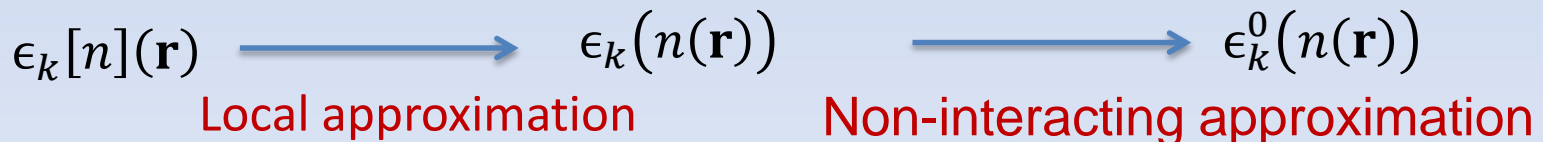
# Early-day DFT: Thomas-Fermi approximation

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

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

$\epsilon_k^0(n(\mathbf{r}))$  : 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)

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

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 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 density, and **here we again adopt the local approximation**.

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

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

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

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

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

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



# Deficiencies of the Thomas-Fermi approximation

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- 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)

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

$$v_X \phi_l(\mathbf{r}) = \int d^3 r' v_X(\mathbf{r}, \mathbf{r}') \phi_l(\mathbf{r}') \approx v_{X\alpha}(\mathbf{r}) \phi_l(\mathbf{r})$$

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



John C. Slater

$\alpha=1 \rightarrow$  Slater local exchange

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

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

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- Hartree-Fock-Slater equation:

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

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

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)

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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 *de facto* the main 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. As a matter of fact, Slater  $X\alpha$  can be better seen as an approximate density functional theory.

# Kohn's thought on the Thomas-Fermi theory

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Now a very crude theory of electronic energy in terms of the electron density distribution,  $n(r)$ , the Thomas-Fermi (TF) theory, had existed since the 1920s<sup>[4] [5]</sup>. It was quite useful for describing some qualitative trends, e.g. for *total* energies 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 had one feature which interested me: It considered interacting electrons moving in an external potential  $v(r)$ , and provided a highly over-simplified one-to-one implicit relation between  $v(r)$  and the density distribution  $n(r)$ :

Walter Kohn, Nobel lecture (1999)

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

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

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

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



Walter Kohn

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

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

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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

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

## 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 potential  $v_{ext}^A(\mathbf{r})$ ,  $v_{ext}^B(\mathbf{r})$ , 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.



# Deduction of the Hohenberg-Kohn theorem I

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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

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A **universal functional** for the energy  $E$  in terms of the density  $n(\mathbf{r})$ ,  $E = E[n]$ , 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 this functional, and the density  $n(\mathbf{r})$  that minimizes the functional is the exact ground state density  $n_0(\mathbf{r})$ .

# Proof of Hohenberg-Kohn Theorem II

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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  $v_{ext}(\mathbf{r})$ .

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

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

# Proof of the Hohenberg-Kohn Theorem II

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

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

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