# **Overview of DFT**

- Classification of first-principles methods
- Hartree-Fock methods
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- Thomas-Fermi-Dirac model
- Density functional theory
- Proof by Levy
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### **Challenges in computational materials science**

- 1. To understand physical and chemical properties of molecules and solids by solving the Dirac equation as accurate as much possible.
- 2. To design novel materials having desired properties from atomistic level theoretically, before actual experiments.
- 3. To propose possible ways of synthesis for the designed materials theoretically.

#### Schrödinger equation and wave functions

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

 $\hat{H} = -\frac{1}{2} \sum_{i=1}^{N_e} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) + \sum_{i=1}^{N_e} \sum_{k=1}^{N_e} \frac{Z_k}{|\mathbf{R}_k - \mathbf{r}_i|} + \sum_{i=1}^{N_e} \sum_{j>i=1}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$ 

Conditions that wave functions must satisfy

(1) indistinctiveness

(2) anticommutation (Pauli's exclusion principle)

(3) orthonormalization

A expression that satisfies above conditions:

$$\Psi = \sum_{I=1} C_I |\phi_{I1}(x_1)\phi_{I2}(x_2)\cdots\phi_{IN_e}(x_{N_e})|$$

Erwin Schrodinger (1887-1961)



### **Classification of electronic structure methods**

Wave function theory	Computational complexity	Features					
e.g., configuration interaction (CI) method							
$\Psi = \sum_{I=1} C_I  \phi_{I1}(x_1)\phi_{I2}(x_2)\cdots\phi_{IN_e}(x_{N_e}) $	O(e <sup>N</sup> )	High accurary High cost					
<b>Density functional theory</b>							
$E(\rho) \qquad \rho(\mathbf{r}) = \sum_{i=1}^{N_e} f(\varepsilon_i) \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})$	<b>O(N<sup>3</sup>)</b>	Medium accuracy Low cost					
Quantum Monte Carlo method							
$\langle E \rangle = \frac{\langle \Psi_{\alpha}   \hat{H}   \Psi_{\alpha} \rangle}{\langle \Psi_{\alpha}   \Psi_{\alpha} \rangle}$	<b>O(N<sup>3~</sup>)</b>	High accuray High cost Easy to parallel					
Many body Green's function method							
$G(t,{\bf r},E)$	<b>O(N<sup>3~</sup>)</b>	Medium accuray Excited states					

#### Hartree-Fock (HF) method

#### **Slater determinantal funtion**

**HF energy** 

$$E_{\rm HF} = \langle \Psi_{\rm HF} | \hat{H} | \Psi_{\rm HF} \rangle$$
  
= 
$$\sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i,j}^{N} (J_{ij} - K_{ij})$$

A form of many electron wave function satisfying indistinctiveness and anticommutation.

**One-electron integral** 

$$H_i = \int \psi_i^*(\mathbf{x}) \left( -\frac{1}{2} \nabla^2 + v(\mathbf{x}) \right) \psi_i^*(\mathbf{x}) d\mathbf{x}$$

**Coulomb integral** 

$$J_{ij} = \int \int \psi_i(\mathbf{x}_1) \psi_i^*(\mathbf{x}_1) \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \psi_j^*(\mathbf{x}_2) \psi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

**Exchange integral** 

$$K_{ij} = \int \int \psi_i^*(\mathbf{x}_1) \psi_j(\mathbf{x}_1) \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \psi_i(\mathbf{x}_2) \psi_j^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

#### The variation of $\Psi$ leads to HF equation:

$$\begin{split} \left( -\frac{1}{2} \nabla^2 + v(\mathbf{x}) \right) \psi_i(\mathbf{x}_1) &+ & \left[ \sum_k^N \int \psi_k(\mathbf{x}_2) \psi_k(\mathbf{x}_2) \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} d\mathbf{x}_2 \right] \psi_i(\mathbf{x}_1) \\ &- \left[ \sum_k^N \int \psi_k(\mathbf{x}_2) \psi_i(\mathbf{x}_2) \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} d\mathbf{x}_2 \right] \psi_k(\mathbf{x}_1) = E_i \, \psi_i(\mathbf{x}_1) \end{split}$$

### **Results by the HF method**

e.g., H <sub>2</sub> O	HF	Experiment
bond(O-H) (Å)	0.940	0.958

Angle(H-O-H) (Deg.)) 106.1 104.5

 $v_1 \text{ (cm}^{-1})$  4070 3657  $v_2 \text{ (cm}^{-1})$  1826 1595

## **Correlation energy**



The correlation energy is about 0.3 % of the total energy.

### **Exchange integral**

By noting one particle wave functions are expressed by a product of spatial one particle and spin functions, we obtain the following formula:

$$K = -\iint d\sigma_{1} d\sigma_{2} \eta_{l}^{*}(\sigma_{1}) \eta_{l'}(\sigma_{1}) \eta_{l}^{*}(\sigma_{2}) \eta_{l'}(\sigma_{2})$$
$$\times \iint d\mathbf{r}_{1} d\mathbf{r}_{2} \phi_{l}^{*}(\mathbf{r}_{1}) \phi_{l'}^{*}(\mathbf{r}_{1}) \frac{1}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} \phi_{l}^{*}(\mathbf{r}_{2}) \phi_{l'}^{*}(\mathbf{r}_{2})$$

If  $\eta_l \neq \eta_{l'} \rightarrow K = 0$  If  $\eta_l = \eta_{l'} \rightarrow K \neq 0$ 

Exchange interaction arises between orbitals with a same spin function.  $\rightarrow$  K<0 in general  $\rightarrow$  Hund's 1<sup>st</sup> rule

### **Two-body distribution function in HF method (1)**

A two-body distribution function is defined by

$$P(\mathbf{r}_{1},\mathbf{r}_{2}) = \frac{N(N-1)}{2} \int \Phi^{*}(x_{1},x_{2},\cdots,x_{N}) \Phi(x_{1},x_{2},\cdots,x_{N}) d\xi_{1} d\xi_{2} dx_{2}\cdots dx_{N}$$
  
$$= \frac{1}{2} \sum_{i\sigma,j\sigma'} \left( |\phi_{i\sigma}(\mathbf{r}_{1})|^{2} |\phi_{j\sigma'}(\mathbf{r}_{2})|^{2} - \delta_{\sigma\sigma'} \phi_{i\sigma}(\mathbf{r}_{2}) \phi_{j\sigma'}(\mathbf{r}_{1}) \phi^{*}_{i\sigma}(\mathbf{r}_{1}) \phi^{*}_{j\sigma'}(\mathbf{r}_{2}) \right)$$

In case of parallel spin  $P_{=}(\mathbf{r}_{1}, \mathbf{r}_{2}) = \frac{1}{2} \sum_{\sigma} n^{\sigma}(\mathbf{r}_{1}) \left( n^{\sigma}(\mathbf{r}_{2}) + n_{x}^{\sigma}(\mathbf{r}_{1}, \mathbf{r}_{2}) \right)$ In case of antiparallel spin  $P_{\neq}(\mathbf{r}_{1}, \mathbf{r}_{2}) = \frac{1}{2} \sum_{\sigma} n^{\sigma}(\mathbf{r}_{1}) n^{-\sigma}(\mathbf{r}_{2})$ In the HF method, electrons with the

different spin are fully independent.

where

Spin density 
$$n^{\sigma}(\mathbf{r}) = \sum_{i}^{\text{occ.}} |\phi_{i\sigma}(\mathbf{r})|^2$$
  
Exchange  
hole density  $n_x^{\sigma}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{|\sum_{i}^{\text{occ.}} \phi_{i\sigma}^*(\mathbf{r}_1)\phi_{i\sigma}(\mathbf{r}_2)|}{n^{\sigma}(\mathbf{r}_1)}$ 

### **Two-body distribution function in HF method (2)**



## Jellium model



V=L<sup>3</sup> Suppose that electrons uniformly occupy in a rectangular unit cell with a lattice constant under periodic boundary condition, and that the positive compensation charges also spread over the unit cell so that the total system can be neutral. (0) (1)

$$\eta_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \eta_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

One-particle wave function

$$\Psi_{\mathbf{k}\lambda}(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k} \cdot \mathbf{r})\eta_{\lambda} \qquad k_i = \frac{2\pi n_i}{L} \qquad n_i = 0, \pm 1, \pm 2, \cdots$$

The second quantized Hamiltonian of the jellium model

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = \sum_{\mathbf{k}\lambda} \frac{k^2}{2} a^{\dagger}_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda} + \frac{1}{2V} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \frac{4\pi}{q^2} \sum_{\lambda_1\lambda_2} a^{\dagger}_{\mathbf{k}+\mathbf{q},\lambda_1} a^{\dagger}_{\mathbf{p}-\mathbf{q},\lambda_2} a_{\mathbf{p}\lambda_2} a_{\mathbf{k}\lambda_1}$$

#### Jellium model in high density limit

Scaled Hamiltonian with mean distance r<sub>s</sub> of electrons

$$\hat{H} = \frac{e^2}{a_0 r_s^2} \left( \sum_{\bar{\mathbf{k}}\lambda} \frac{1}{2} \bar{\mathbf{k}}^2 a_{\bar{\mathbf{k}}\lambda}^{\dagger} a_{\bar{\mathbf{k}}\lambda} + \frac{r_s}{2\bar{V}} \sum_{\bar{\mathbf{k}}\bar{\mathbf{p}}\bar{\mathbf{q}}} \sum_{\lambda_1\lambda_2} \frac{4\pi}{\bar{\mathbf{q}}^2} a_{\bar{\mathbf{k}}+\bar{\mathbf{q}}\lambda_1}^{\dagger} a_{\bar{\mathbf{p}}-\bar{\mathbf{q}}\lambda_2}^{\dagger} a_{\bar{\mathbf{p}}\lambda_2} a_{\bar{\mathbf{p}}\lambda_2} a_{\bar{\mathbf{k}}\lambda_1} \right)$$

 $r_s \rightarrow 0$  corresponds to the high density limit, and the second term becomes a small perturbation. Thus, the first term gives the zeroth order energy, while the second term gives the first order correction in the perturbation theory.

$$\begin{split} E &= E_0 + E_1 \\ E_0 &= \langle F | H_0 | F \rangle \\ E_1 &= \langle F | H_1 | F \rangle \end{split} \qquad \hat{H}_0 = \sum_{\mathbf{k}\lambda} \frac{1}{2} \mathbf{k}^2 a_{\mathbf{k}\lambda}^{\dagger} a_{\mathbf{k}\lambda} \\ \hat{H}_1 &= \frac{e^2}{2V} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \sum_{\lambda_1\lambda_2} \frac{4\pi}{\mathbf{q}^2} a_{\mathbf{k}+\mathbf{q}\lambda_1}^{\dagger} a_{\mathbf{p}-\mathbf{q}\lambda_2}^{\dagger} a_{\mathbf{p}\lambda_2} a_{\mathbf{p}\lambda_2} a_{\mathbf{k}\lambda_1} \end{split}$$

#### **Energies in the jellimum model**

The evaluation of  $E_0$  and  $E_1$  is cumbersome, but possible analytically, and as the result we obtain the following formulae:



These results are very important, because they suggest that the total energy seems to be expressed by electron density, leading to a birth of a density functional theory.

## Local density approximation (LDA)

An energy of the system is approximated by employing a local energy density which is a function of the local density  $\rho$ .



### Thomas-Fermi model: The simplest density functional

Local density approximation (LDA) to the kinetic energy. No exchange-correlation

$$E_{\rm TF} = \int \rho(\mathbf{r}) t(\rho) d\mathbf{r} + \int \rho(\mathbf{r}) v_{\rm ext} d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + \sum_{I,J} \frac{Z_I Z_J}{|\mathbf{R}_1 - \mathbf{R}_2|}$$
$$t(\rho) = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \rho^{\frac{2}{3}}$$

The kinetic energy density  $t(\rho)$  is that of non-interacting electrons in the jellium model. The second quantized Hamiltonian of the jellium model

$$\hat{H} = \hat{H}_{0} + \hat{H}_{1} = \sum_{\mathbf{k}\lambda} \frac{k^{2}}{2} a_{\mathbf{k}\lambda}^{\dagger} a_{\mathbf{k}\lambda} + \frac{1}{2V} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \frac{4\pi}{q^{2}} \sum_{\lambda_{1}\lambda_{2}} a_{\mathbf{k}+\mathbf{q},\lambda_{1}}^{\dagger} a_{\mathbf{p}-\mathbf{q},\lambda_{2}}^{\dagger} a_{\mathbf{p}\lambda_{2}} a_{\mathbf{k}\lambda_{1}}$$

$$\frac{E^{(0)}}{N} = \frac{1}{N} \langle F | \hat{H}_{0} | F \rangle$$

$$= \frac{1}{2N} \sum_{\mathbf{k}\lambda} k^{2} \langle F | \hat{n}_{\mathbf{k}\lambda} | F \rangle$$

$$= \frac{1}{2N} \sum_{\mathbf{k}\lambda} k^{2} \theta (k_{F} - k)$$

$$= \frac{3}{10} (3\pi)^{\frac{2}{3}} \rho^{\frac{2}{3}}$$

### **Thomas-Fermi-Dirac model**

LDA to the kinetic and exchange, but no correlation

The first order perturbation energy in the jellium model is used as the exchange energy density  $\varepsilon_x(\rho)$ .

The second quantized Hamiltonian of the jellium model

$$\hat{H} = \hat{H}_{0} + \hat{H}_{1} = \sum_{\mathbf{k}\lambda} \frac{k^{2}}{2} a_{\mathbf{k}\lambda}^{\dagger} a_{\mathbf{k}\lambda} + \frac{1}{2V} \sum_{\mathbf{k}pq} \frac{4\pi}{q^{2}} \sum_{\lambda_{1}\lambda_{2}} a_{\mathbf{k}+\mathbf{q},\lambda_{1}}^{\dagger} a_{\mathbf{p}-\mathbf{q},\lambda_{2}}^{\dagger} a_{\mathbf{p}\lambda_{2}} a_{\mathbf{k}\lambda_{1}}$$

$$\frac{E^{(1)}}{N} = \frac{1}{N} \langle F|\hat{H}_{1}|F\rangle$$

$$= \frac{1}{2NV} \sum_{\mathbf{k}pq} \sum_{\lambda_{1}\lambda_{2}} \frac{4\pi}{q^{2}} \langle F|a_{\mathbf{k}+\mathbf{q},\lambda_{1}}^{\dagger} a_{\mathbf{p}-\mathbf{q},\lambda_{2}}^{\dagger} a_{\mathbf{p}\lambda_{2}} a_{\mathbf{k}\lambda_{1}}|F\rangle$$

$$= -\frac{1}{2NV} \sum_{\lambda_{1}} \sum_{\mathbf{k}q} \frac{4\pi}{q^{2}} \theta(k_{F} - |\mathbf{k}+\mathbf{q}|) \theta(k_{F} - k|)$$

$$= -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho^{\frac{1}{3}}$$

### **Failures of Thomas-Fermi-Dirac model**



by W.Yang, 1986

No shell structure of atoms
 No binding of atoms
 Negative ion is unstable
 The failures may be attributed to the large error in the kinetic energy functional.

The kinetic energy (a.u.) of Ar(a.u.)

HF <sup>a</sup>	526.82
TF <sup>b</sup>	489.95
KS-LDA	525.95

a: Cemency-Roetti (1974) b: Mrphy-Yang (1980)

### **Hohenberg-Kohn's theorem**

#### The first theorem

The energy of non-degenerate ground state can be expressed by a functional of electron density.

$$E[\rho] = \int \rho(\mathbf{r})v(\mathbf{r})d + T[\rho] + J[\rho] + E_{xc}[\rho]$$
  
The second theorem  $F_{HK}[\rho]$ 



W.Kohn (1923-)

The ground state energy can be obtained by minimizing the functional with respect to electron density.

$$E[\rho] < E[\tilde{\rho}]$$

Hohenberg and Kohn, PR 136, B864.

### The proof of the first theorem by HK

Suppose that different vs give the same  $\rho$ .

$$\begin{split} \hat{H} &= \hat{T} + v \longrightarrow \hat{H}\Psi = E\Psi \\ \hat{H}' &= \hat{T} + v' \longrightarrow \hat{H}'\Psi' = E'\Psi' & \rho \\ E &< \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | (\hat{H} - \hat{H}') | \Psi' \rangle \\ &= E' + \int \rho(\mathbf{r})(v(\mathbf{r}) - v'(\mathbf{r})) d\mathbf{r} \\ E' &< \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | (\hat{H}' - \hat{H}) | \Psi \rangle \\ &= E - \int \rho(\mathbf{r})(v(\mathbf{r}) - v'(\mathbf{r})) d\mathbf{r} \end{split}$$

Adding above two equations leads to

$$E + E' < E + E'$$

#### A discrepancy occurs. Thus, for a given v, $\rho$ is uniquely determined.

It was assumed the v-representability that a corresponding v exists for a given  $\rho$ . Later the proof was modified under the N-representability condition by Levy (1979).

### The proof of the second theorem by HK

According to the first theorem and the variational principle,

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_{\mathrm{HK}}[\tilde{\rho}] \ge E[\rho]$$

#### Thus,

$$E[\rho] < E[\tilde{\rho}]$$

By the proof of the HK's theorem, the TF and TFD models have been regarded as approximate theories for the rigorous DFT.

### v- and N-representability (1)

The proof for the first HK theorem shows

but never show

$$v \rightarrow \rho \quad \cdots \quad (A)$$
  
 $v \leftarrow \rho \quad \cdots \quad (B)$ 

If the condition (B) is satisfied for a given  $\rho$ , it is mentioned that the density  $\rho$  is v-representable. In the HK theorem we assumed the v-representability implicitly.

On the other hand, if the following condition (C) is satisfied for a given  $\rho$ , it is mentioned that the density  $\rho$  is N-representable.



### v- and N-representability (2)

Condition of v-representability

For general cases, the condition is unknown.

Condition of N-representability

Gilbert, PRB 12, 2111 (1975).

Positivity Charge conservation Continuity  $\rho(\mathbf{r}) \ge 0 \qquad \int \rho(\mathbf{r}) d\mathbf{r} = N \qquad \int \left| \nabla \rho(\mathbf{r})^{1/2} \right|^2 d\mathbf{r} < \infty$ 

The condition of N-representability is physically reasonable, and easy to hold. Thus, it would be better to formulate DFT under the N-representability, which was actually done by Levy in 1979.

### **Theorem by Levy**

Theorem I: The ground state energy  $E_{GS}$  is the lower bound of  $E[\rho]$ .

$$E[\rho] = F[\rho] + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$
$$F[\rho] = \min_{\Psi \to \rho} \langle \Psi | (\hat{T} + \hat{V}_{\text{ee}}) | \Psi \rangle$$

Theorem II: The ground state energy  $E_{GS}$  is represented by the ground state one-electron density  $\rho_{GS}$ .

$$E_{\rm GS} = \int v_{\rm ext}(\mathbf{r})\rho_{\rm GS}(\mathbf{r})d\mathbf{r} + F[\rho_{\rm GS}]$$

Levy, PNAS 76, 6062 (1979)

### **Proof of the theorem by Levy**

Let us consider a constraint minimization of E.

$$E_{\rm GS} = \min_{\Psi} \langle \Psi | (\hat{T} + \hat{V}_{\rm ee} + v_{\rm ext}) | \Psi \rangle$$
  
$$= \min_{\rho} \left\{ \min_{\Psi \to \rho} \langle \Psi | (\hat{T} + \hat{V}_{\rm ee} + v_{\rm ext}) | \Psi \rangle \right\}$$
  
$$= \min_{\rho} \left\{ \min_{\Psi \to \rho} \langle \Psi | (\hat{T} + \hat{V}_{\rm ee}) | \Psi \rangle + \int v_{\rm ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\}$$
  
$$= \min_{\rho} \left\{ F[\rho] + \int v_{\rm ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\}$$
 The theorem 1

The first line is just a conventional variational problem with respect to  $\psi$ .

In the second line, two step minimization is introduced.

- (1) Choose N-representable p
- (2) Minimize E with respect to  $\psi$  giving  $\rho \min_{\Psi \to \rho}$
- (3) Repeat steps (1), (2) min

The third line is a transformation of the second line. The fourth line is a transformation of the third line.

The theorem 1 is proven by the first = the fourth line.

The ground state density  $\rho_{GS}$  is N-representative, implying that it is included in the domain. Thus, the fourth line proves the theorem 2.

### Kohn-Sham equation (1)

Since the kinetic energy functional in the TFD model is a crude model, the majority part of the kinetic energy is evaluated by that of a non-interacting system.

$$\begin{split} E[\rho] &= T[\rho] + J[\rho] + \int \rho v_{\text{ext}} d\mathbf{r} + E_{\text{xc}}^{(0)}[\rho] \\ &= T_s + J[\rho] + \int \rho v_{\text{ext}} d\mathbf{r} + (T[\rho] - T_s) + E_{\text{xc}}^{(0)}[\rho] \\ &= T_s + J[\rho] + \int \rho v_{\text{ext}} d\mathbf{r} + E_{\text{xc}}[\rho] \end{split}$$

$$\begin{aligned} \text{The kinetic energy of non-interacting electrons} \\ T_s &= -\frac{1}{2} \sum_{i=1}^{\text{occ}} \int \phi_i \nabla^2 \phi_i d\mathbf{r} \end{aligned}$$

The wave functions of non-interacting electrons are evaluated by an one-particle KS eq. under an effective potential. Then, the electron density of non-interacting electrons becomes equal to that of the true wave functions.

$$\frac{\delta E}{\delta \phi} = 0 \qquad \begin{aligned} \hat{H}_{\rm KS} \phi_i &= \varepsilon_i \phi_i \\ \hat{H}_{\rm KS} &= -\frac{1}{2} \nabla^2 + v_{\rm eff} \end{aligned}$$

KS effective potential

$$\begin{aligned} v_{\text{eff}} &= v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})} \\ v_{\text{Hartree}}(\mathbf{r}) &= \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \end{aligned}$$

Comparison of the kinetic energy of Ar HFa 526.82 a: Cemency-Roetti (1974) b: Mrphy-Yang (1980) HFa 526.82 in a.u.

**Proof of** 
$$\frac{\delta E}{\delta \rho} = 0$$

### KS eq. is derived by assuming $\delta E/\delta \phi = 0$ . However, how about $\delta E/\delta \rho = 0$ ?

By expressing the kinetic energy as

$$T_s = \sum_i n_i \epsilon_i - \int \rho(\mathbf{r}) v_{\text{eff}}(\mathbf{r}) d\mathbf{r}.$$

and considering variation of each term, we have the following eq.

$$\delta E[\rho] = \int d\mathbf{r} \delta \rho(\mathbf{r}) \left( v(\mathbf{r}) + \int d\mathbf{r}' \frac{\delta v_{\text{eff}}(\mathbf{r}')}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}') - v_{\text{eff}}(\mathbf{r}) - \int d\mathbf{r}' \rho(\mathbf{r}') \frac{\delta v_{\text{eff}}(\mathbf{r}')}{\delta \rho(\mathbf{r})} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})} \right).$$

To satisfy  $\delta E=0$  for arbitrary  $\delta \rho$ , the following relation should be satisfied:  $v_{\text{eff}} = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r})$ 

This is nothing but the definition of the KS effective potential. Thus,  $\rho$  calculated by the KS eq. satisfies  $\delta E/\delta \rho=0$ , which might be the density of the ground state.

## **Eigenvalue of KS eq.**

The physical meaning of eigenvalues  $\varepsilon$  is non-trivial, since  $\varepsilon$  were introduced as Lagrange's multipliers.

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right)\psi_i(\mathbf{x}) = \epsilon_i\psi_i(\mathbf{x})$$
$$v_{\text{eff}}(\mathbf{r}) = -\sum_{\alpha}\frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} + \int\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}$$

Mathematically, the eigenvalue  $\varepsilon_i$  is the partial derivative of the total energy w. r. t.  $n_i$ .

Janak's theorem  $\frac{\partial E}{\partial n_i} = \varepsilon_i$ 

### **Derivation of Janak's theorem**

By noting that the charge density is determined by  $\{n_k\}$  and  $\{\psi_k\}$ ,

$$\rho(\mathbf{r}) = \sum_{i=1}^{n} n_i |\psi_i(\mathbf{r})|^2$$

it is found that the variation of total energy is given by

$$\delta E[\{n_k\}, \{\psi_k\}] = \sum_k \int d\mathbf{r} \left(\frac{\delta E}{\delta \psi_k}\right)_n \delta \psi_k + \sum_k \left(\frac{\partial E}{\partial n_k}\right)_{\psi} \delta n_k,$$

The first term of the right hand side is zero because of the derivation of KS equation, thus we have

$$\begin{split} \frac{\partial E}{\partial n_i} &= \left(\frac{\partial E}{\partial n_i}\right)_{\psi}, \\ &= \int d\mathbf{r} \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla\right) \psi_i(\mathbf{r}) + \int d\mathbf{r} \frac{\delta}{\delta \rho(\mathbf{r})} \left\{J[\rho(\mathbf{r})] + E_{\rm xc}[\rho] + \int d\mathbf{r}' v(\mathbf{r})\rho(\mathbf{r})\right\} \frac{\partial n(\mathbf{r})}{\partial n_i}, \\ &= \int d\mathbf{r} \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla\right) \psi_i(\mathbf{r}) + \int d\mathbf{r} \psi_i^*(\mathbf{r}) v_{\rm eff}(\mathbf{r}) \psi_i(\mathbf{r}), \\ &= \epsilon_i \end{split}$$

#### **Comparison between experiment and theory**

STS (scanning tunneling spectroscopy) for SWCNT

Avramov et al., CPL 370, 597 (2003).

Semiconducting SWCNT



Fig. 2. The STS experimental normalized conductance (V/I)(dI/dV) - V [3] (a) and theoretical (b) PBE and PBE0 DOS of semiconducting chiral (14,3) SWNT.

Fig. 3. The STS experimental conductance dI/dV - V [1] (solid line) and theoretical (dashed lines) PBE and PBE0 DOS of metallic zigzag (15,0), (12,0) and (9,0) SWNTs.

One can see the crude approximation works well expect for the band gap of SWCNTs.





#### d-band width: Theory vs. Expt.

Angle resolved photoemission for transition metals

Eastman et al., PRL 44, 95 (1980)

Though LDA calculations qualitatively reproduce the d-band width of 3d-transition metals, however, the calculations overestimate the values about 1eV.



FIG. 4. Occupied *d*-band widths (eV) and magnetic exchange splittings (293 K). The widths are at the symmetry points P, L, L, and X, and at X for Fe, Co, Ni, and Cu, respectively, while the exchange splittings are at P,  $\Gamma$ , and near L for Fe, Co, and Ni, respectively. Theoretical widths are taken from Ref. 1. For Co, experimental exchange splittings are 0.9 ( $\Gamma_{12}$ ) and 1.2 ( $\Gamma_{25}$ ) eV. An average value is given in Fig. 4. Experimental accuracies are about  $\pm$  0.2 eV.

### **Approximation to E**<sub>xc</sub>

In the KS method, once we know  $E_{xc}[\rho]$ , the ground state of the system can be obtained. However, as this quantity contains all the details of electron correlation, a universal functional has been still under development. In most of practical DFT calculations,

LDA (Local Density Approximation) or GGA (Generalized Gradient Approximation) is employed. In LDA,  $E_{xc}[\rho]$  is given by

$$E_{\rm xc}[\rho] = \int \varepsilon_{\rm xc}(\rho(\mathbf{r}))\rho(\mathbf{r})dr$$

 $\varepsilon_{xc}$  is an exchange-correlation energy density of jellium model with the electron density  $\rho$ .

### **Correlation energy in Jellium model**

In Jellium model 
$$t(\rho) = \frac{3}{10}(3\pi)^{\frac{2}{3}}\rho^{\frac{2}{3}} \qquad \varepsilon_{x}(\rho) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{1}{3}}$$

The exact analytic formula of  $\varepsilon_c(\rho)$  is unknown.

It is numerically evalulated by QMC, and it is fitted to analytical functions.

QMC D. M. Ceperley and B. J. Alder, Phys. Rev. Lett., 45, 566 (1980)

Analytical formula by fitting S.H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980)

$$\begin{split} \varepsilon_c &= A \left\{ \ln \frac{x^2}{X(x)} + \frac{2b}{Q} \tan^{-1} \frac{Q}{2x+b} - \frac{bx_0}{X(x_0)} \left[ \ln \frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q} \tan^{-1} \frac{Q}{2x+b} \right] \right\} \\ r_s &= \left( \frac{4\pi}{3} \rho \right)^{-1/3} \qquad A = 0.0310907 \\ x &= r_s^{1/2} \qquad b = 3.72744 \qquad \varepsilon_c \quad \textbf{-0.05} \\ Q &= (4c-b^2)^{1/2} \qquad c = 12.9352 \\ X(x) &= x^2 + bx + c \qquad x_0 = -0.10498 \qquad \textbf{-0.10498} \end{split}$$

#### **Accuracy of KS-LDA**

Geometry of molecules and bulks

Error of 1-5 %

**Cohesive energy** 

Error of 0.1-0.5 eV

**Dipole moment** 

Error of 10 %

In spite of the crude approximation by LDA, the results look good.

**Excitation energy** 

Underestimation of 50%

vdW energy

Not in tolerable range

### **General consideration to LDA (1)**

LDA is based on the assumption that each part of the system can be locally regarded as a homogeneous electron gas with the local electron density  $\rho(r)$ . This condition is mathematically expressed as

$$abla 
ho(\mathbf{r}) rac{2\pi}{k_{
m F}(\mathbf{r})} << 
ho(\mathbf{r}) \qquad \cdots \qquad ({
m A})$$

with  $k_{\rm F}(\mathbf{r}) = \{3\pi^2 \rho(\mathbf{r})\}^{1/3}$  the local Fermi wave vector.

The left hand side of Eq. (A) is the change in the electron density over the Fermi wave length, which should be much smaller than the electron density itself for the validity of LDA.

It is known that Eq. (A) is not satisfied in real systems. Nevertheless, it is also known from many examples that LDA works much better than expected. Why?

## **General consideration to LDA (2)**

There are mainly two reasons why LDA works much better than expected.

#### **1. ΔSCF**

In most cases, we only need the difference in total energy between different situations. For example, the energy difference between the structures A and B. Then the common error of LDA cancels out. This is a nice aspect of variational principle.

#### **1. Sum rule in the xc hole density**

As the total energy is an integrated quantity over the space, only the spherical average of xc hole density affects to the total energy. The sum rule of the xc hole is an important factor.

A B ← LDA error

#### **Exchange-correlation hole**

#### **Exchange energy**

The Coulomb interaction between and electron and exchange hole whose integral gives -1.

$$E_{\mathbf{x}} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho_{\mathbf{x}}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \qquad \int \rho_{\mathbf{x}}(\mathbf{r}_1,\mathbf{r}_2) d\mathbf{r}_2 = -1$$

#### **Correlation energy**

The Coulomb interaction between and electron and correlation hole whose integral give zero.

$$E_{\rm c} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho_{\rm c}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \qquad \int \rho_{\rm c}(\mathbf{r}_1,\mathbf{r}_2) d\mathbf{r}_2 = 0$$

An important consequence is that only the spherical average of exchange-correlation hole can attribute to the xc energy.

$$E_{\rm xc} = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int_0^\infty 4\pi s ds \rho_{\rm xc}^{\rm SA}(\mathbf{r},s)$$

#### **Exchange hole of Ne and its spherical average**



O. Gunnarson et al., PRB 20, 3136 (1979)

### **Deficiencies of LDA**

- 1. The band gap of solid is underestimated about 50%.
- 2. vdW interaction is not described properly.
- 3. The lattice constant is underestimated by a few %.
- 4. Poor description of 3d transition metals: strucutre and magnetism
- 5. The activation barrier of chemical reaction is largely underestimated.
- 6. Orbital polarization of transition metal oxides is not described.

## GGA by Perdew, Burke, and Ernzerhof (PBE)

PRL 77, 3865 (1996).

They developed a GGA functional which satisfies several conditions such as (1) the sum rule for exchange and correlation holes, (2) the asymptotic forms at  $s \rightarrow 0$ .

It can be written as 
$$E_{\rm XC}^{\rm GGA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r \, n \, \epsilon_{\rm X}^{\rm unif}(n) F_{\rm XC}(r_s, \zeta, s).$$
  
 $\epsilon_{\rm X}^{\rm unif} = -3e^2 k_F / 4\pi < 0$ 

$$s = |\nabla n|/2k_F n$$
  

$$\zeta = (n_{\uparrow} - n_{\downarrow})/n$$
  

$$n = 3/4\pi r_s^3$$

For the most of real materials,  $r_s$  ranges from 2 to 6. Then,  $F_{xc}$  increases with *s*, i.e.,  $E_{xc}$  more negative with the increasing *s*.

For most physical  $r_s$ , GGA favors density inhomogeneity more than LDA does.



## LDA vs GGA: p of Ne

At two shell structures, GGA favors more localized states. GGA favors density inhomogeneity $\rightarrow$  localized states are favored.



### LDA vs GGA: Atomic calculations by GGA-PBE

#### Exchange energy (-Ex, in Ha)

Atom	Exact	LSDA	PBE		
H	0.3125	0.2680	0.3059		
He	1.0258	0.8840	1.0136		
Be	2.6658	2.3124	2.6358		
N	6.6044	5.908	6.5521		
Ne	12.1050	11.0335	12.0667		
Error, %	0	9.8	0.8		

#### Correlation energy (-Ex, in Ha)

Atom	Exact	LSDA	PBE
Н	0.0000	0.0222	0.0060
He	0.0420	0.1125	0.0420
Be	0.0950	0.2240	0.0856
N	0.1858	0.4268	0.1799
Ne	0.3939	0.7428	0.3513
Error, %	0	128.3	6.4

The tables were taken from R.M. Martin, "Electronic Structure".

# The significant improvement for $E_x$ and $E_c$ was made by GGA.

### LDA vs. GGA: Cohesive properties of Iron

Asada and Terakura, PRB 46, 13599 (1992).

GGA reproduces the experimental ground state (FM-bcc), while LDA predicts the NM-hcp state as the ground state.



### **Comparison between LDA and GGA: Structural properties of bulks**

	a_0			$B_0$			•		
Solid	LDA	PBE	WC	Expt. <sup>a</sup>	LDA	PBE	WC	Expt. <sup>a</sup>	
Li (A2)	3.363	3.435	3.449	3.477	15.2	14.0	13.4	13.0	-
C (A4)	3.536	3.575	3.558	3.567	469	434	451	443	
C (A9)	2.447	2.471	2.460	2.464					
Na (A2)	4.047	4.196	4.199	4.225	9.41	7.85	7.32	7.5	
Al (A1)	3.983	4.041	4.023	4.047	84.3	79.2	80.6	73	
Si (A4)	5.407	5.475	5.437	5.430	96.4	88.7	94.0	99.2	
K (A2)	5.045	5.282	5.256	5.225	4.50	3.61	3.49	3.7	
Ca (A1)	5.333	5.530	5.458	5.58	18.7	17.3	17.4	15	
V (A2)	2.932	3.001	2.965	3.03	213	183	198	162	
Fe (A2)	2.753	2.830	2.791	2.868	256	194	227	167	
Ni (A1)	3.423	3.518	3.468	3.524	259	200	231	184	F. Tran et al.,
Cu (A1)	3.522	3.632	3.573	3.615	191	141	168	133	PRB 75, 115131
Ge (A4)	5.632	5.769	5.686	5.652	72.7	59.5	67.8	75.8	(2007)
Rb (A2)	5.374	5.670	5.609	5.59	3.59	2.77	2.71	3.06	(2007).
Sr (A1)	5.786	6.027	5.914	6.08	14.4	11.4	12.2	12	
Nb (A2)	3.250	3.312	3.280	3.30	193	171	183	170	
Mo (A2)	3.116	3.164	3.139	3.15	294	260	279	272	
Rh (A1)	3.759	3.834	3.795	3.798	320	259	292	269	
Pd (A1)	3.848	3.948	3.892	3.881	231	170	207	195	
Ag (A1)	4.007	4.152	4.065	4.069	140.4	91.0	118.9	109	
Sn (A4)	6.481	6.661	6.548	6.481	45.7	36.3	42.4	53	

GGA-PBE: Error in  $a_0$ : ~ 0.03 Å, in  $B_0$ : ~ 10 GPa

## **Successes and failures of GGA**

#### **Successes:**

1. Accuracy:

Atomization energy: Bond length: Bulk modulus: Energy barrier: Mean absolute error 0.3 eV (mostly overbinding) Overestimation of 1 % Underestimation of 5 % Underestimation of 30 %

2. Accurate description of hydrogen bonding3. Better description of magnetic ground states (e.g., bcc Fe)

#### **Failures:**

Band gap:
 vdW interaction:
 Strongly correlation:

Underestimation of 30 % No binding in many cases No orbital polarization of localized d- and f-states

### **Beyond GGA**

#### 1. Hybrid functional

Exact exchange is admixed with GGA, leading to a better description for the band gap problem.

#### 2. Non-local correlation functional

A fully non-local functional based on the Adiabatic Connection/Fluctuation Dissipation Theorem (AC/FDT). This well reproduces accurate CCSD(T) results for vdW systems.

#### 2. Orbital dependent functional (DFT+U method)

Strong correlation in localized orbitals appearing transition metal oxides is taken into account by adding a Hubbard term.

### General consideration of eigenvalues in the HF method and GGA



V<sub>eff</sub> consisting of N-1

# Band gap by a hybrid functional



The **HF method** overestimates the gap due to lack of screening effect.

**GGA** underestimates the gap due to self-interaction error.

The **hybrid functional (HSE)** can well reproduce the experimental band gap of insulators and semiconductors due to inclusion of a proper screening effect, which are well compared to results by a many body perturbation theory, **GW method**.

Paier et al., JCP 124, 154709 (2006). Heyd et al., JCP 121, 1187 (2004). Shishkin et al., PRB 75, 235102 (2007). Shimazaki et al., JCP 132, 224105 (2005).

## vdW interaction

A fully non-local functional developed by Langreth et al., which is based on the Adiabatic Connection/Fluctuation Dissipation Theorem (AC/FDT), well reproduces accurate CCSD(T) results.



### General consideration of Self-interaction and orbital polarization

Consider degenerate states are partially filled e.g., dorbitals in oxides.

In case that three degenerate states are occupied by two electrons, the occupation of 2/3 for each state is energetically favored if there is spurious selfinteraction. If there is no spurious interaction, a naïve consideration implies that the left case leads to interaction of 8/3(=3\*2/3\*4/3), while in right case the interaction of 2(=2\*1\*1).





#### **Orbital polarization of localized d-electrons: Importance of orbital dependent functional**

$$E_U = \frac{1}{2} \sum_{\alpha} (U_{\alpha} - J_{\alpha}) \sum_{\sigma} \{ \operatorname{Tr}(n_{\alpha}^{\sigma}) - \operatorname{Tr}(n_{\alpha}^{\sigma} n_{\alpha}^{\sigma}) \}.$$

The functional is discontinuous at occupation numbers of integer, which should be hold in an exact functional.

-2

0

LDA

2

 $Co^{2+:} d^7$ 

eg

t<sub>2g</sub>

7

5

3

1

-8

-6

DOS(States/atom spin)



0,25 0.2 Han et al., PRB 73, 045110 (2006).

## Summary

We have discussed the following issues related DFT.

- Classification of first-principles methods
- Hartree-Fock methods
- Jellium model
- Local density appoximation
- Thomas-Fermi-Dirac model
- Density functional theory
- Proof by Levy
- Kohn-Sham equation
- Janak's theorem
- LDA and GGA
- Beyond GGA

I think that there is still a plenty of room for development of DFT.

- Exchange-correlation functionals
- DFT for excited states
- Large-scale DFT methods