Fundamentals of 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

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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 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

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

kinectic   external   e-e

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

Erwin Schrodinger
(1887-1961)

Conditions that wave functions must satisfy

(1) indistinctiveness
(2) anticommutation (Pauli's exclusion principle)
(3) orthonormalization

A expression that satisfies above conditions:

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

Classification of electronic structure methods

	Computational complexity	Features

Wave function theory

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^N) — High accurary / High cost

Density functional theory

$$E(\rho) \quad \rho(\mathbf{r}) = \sum_{i=1}^{N_e} f(\varepsilon_i)\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$$

O(N³) — Medium accuracy / Low cost

Quantum Monte Carlo method

$$\langle E \rangle = \frac{\langle \Psi_\alpha | \hat{H} | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle}$$

O(N³~) — High accurary / High cost / Easy to parallel

Many body Green's function method

$$G(t, \mathbf{r}, E)$$

O(N³~) — Medium accurary / Excited states

Hartree-Fock (HF) method

Slater determinantal funtion

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \cdots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \cdots & \psi_N(x_2) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \psi_1(x_N) & \psi_2(x_N) & \cdots & \psi_N(x_N) \end{vmatrix}$$

A form of many electron wave funtion satisfying indistinctiveness and anti-commutation.

HF energy

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

One-electron integral

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

Coulomb integral

$$J_{ij} = \int \int \psi_i(x_1)\psi_i^*(x_1)\frac{1}{|x_1 - x_2|}\psi_j^*(x_2)\psi_j(x_2)dx_1 dx_2$$

Exchange integral

$$K_{ij} = \int \int \psi_i^*(x_1)\psi_j(x_1)\frac{1}{|x_1 - x_2|}\psi_i(x_2)\psi_j^*(x_2)dx_1 dx_2$$

The variation of E w.r.t ψ leads to HF equation:

$$\left(-\frac{1}{2}\nabla^2 + v(x) \right) \psi_i(x_1) + \left[\sum_k^N \int \psi_k(x_2)\psi_k(x_2)\frac{1}{|x_1 - x_2|}dx_2 \right] \psi_i(x_1)$$

$$- \left[\sum_k^N \int \psi_k(x_2)\psi_i(x_2)\frac{1}{|x_1 - x_2|}dx_2 \right] \psi_k(x_1) = E_i \psi_i(x_1)$$

Results by the HF method

e.g., H$_2$O

	HF	Experiment
bond(O-H) (Å)	0.940	0.958
Angle(H-O-H) (Deg.))	106.1	104.5
ν_1 (cm^{-1})	4070	3657
ν_2 (cm^{-1})	1826	1595

Correlation energy

$$E_{corr} = E_{exact} - E_{HF}$$

e.g.

H_2O
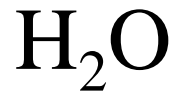
$$E_{exact} = -76.0105 \text{ a.u.}$$
$$E_{corr} = -0.1971 \text{ a.u.}$$

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

Exchange interaction arises between orbitals with a same spin funcion.   → K<0 in general → Hund's 1st 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
$$n_x^{\sigma}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{|\sum_i^{\text{occ.}} \phi_{i\sigma}^*(\mathbf{r}_1) \phi_{i\sigma}(\mathbf{r}_2)|^2}{n^{\sigma}(\mathbf{r}_1)}$$

Two-body distribution function in HF method (2)

Exchange hole density

$$n_x^\sigma(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\left|\sum_i^{\text{occ.}} \phi_{i\sigma}^*(\mathbf{r}_1)\phi_{i\sigma}(\mathbf{r}_2)\right|^2}{n^\sigma(\mathbf{r}_1)}$$

Pauli's exclusion principle

$$n_x^\sigma(\mathbf{r}_1, \mathbf{r}_1) = -n^\sigma(\mathbf{r}_1) \qquad \longrightarrow \qquad P_=(\mathbf{r}_1, \mathbf{r}_1) = 0$$

Sum rule

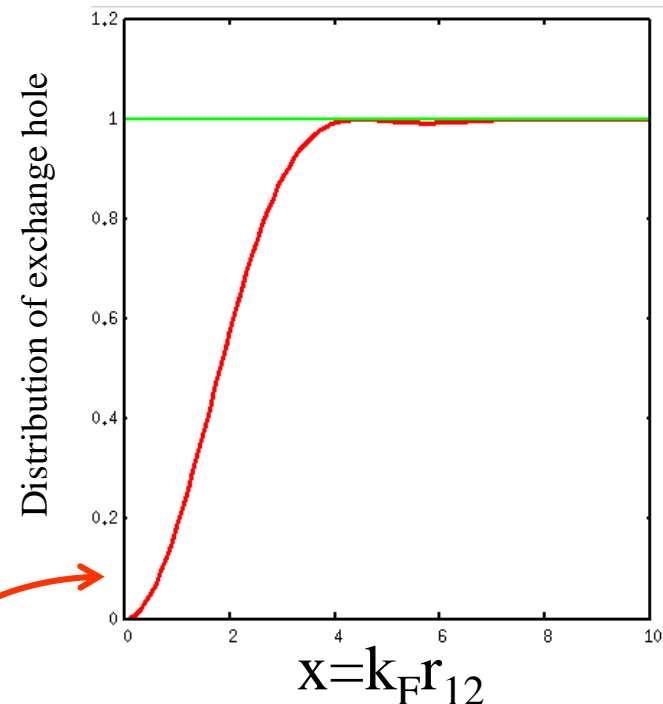$$\int n_x^\sigma(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = -1$$

Exchange hole density for Jellium model

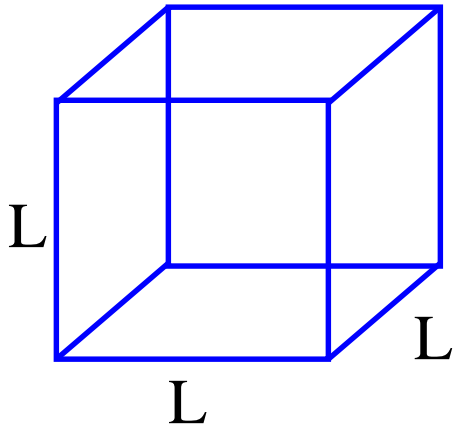$$n_x^\sigma(\mathbf{r}_1, \mathbf{r}_2) = -\frac{9}{2}n\left(\frac{j_1(k_F r_{12})^2}{k_F r_{12}}\right)$$

$$k_F = (3\pi^2 n)^{1/3}$$

In case of non-spin polarization, $n^\sigma(\mathbf{r}) = n/2$

$$P_=(\mathbf{r}_1, \mathbf{r}_2) = \frac{n^2}{2}\left[1 - 9\left(\frac{j_1(k_F r_{12})^2}{k_F r_{12}}\right)\right]$$

Distribution of exchange hole

$x = k_F r_{12}$

Jellium model

$V=L^3$

L

L

L

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.

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

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_s of electrons

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

$r_s \rightarrow 0$ 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.

$$E = E_0 + E_1$$

$$E_0 = \langle F | H_0 | F \rangle$$

$$E_1 = \langle F | H_1 | F \rangle$$

$$\hat{H}_0 = \sum_{\mathbf{k}\lambda} \frac{1}{2}\mathbf{k}^2 a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda}$$

$$\hat{H}_1 = \frac{e^2}{2V}\sum_{\mathbf{kpq}}\sum_{\lambda_1\lambda_2}\frac{4\pi}{\mathbf{q}^2} a_{\mathbf{k}+\mathbf{q}\lambda_1}^\dagger a_{\mathbf{p}-\mathbf{q}\lambda_2}^\dagger a_{\mathbf{p}\lambda_2} a_{\mathbf{k}\lambda_1}$$

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:

Kinetic energy

$$\frac{E_0}{N} = \frac{3e^2 a_0}{10}\left(3\pi^2\right)^{2/3} \rho^{2/3}$$
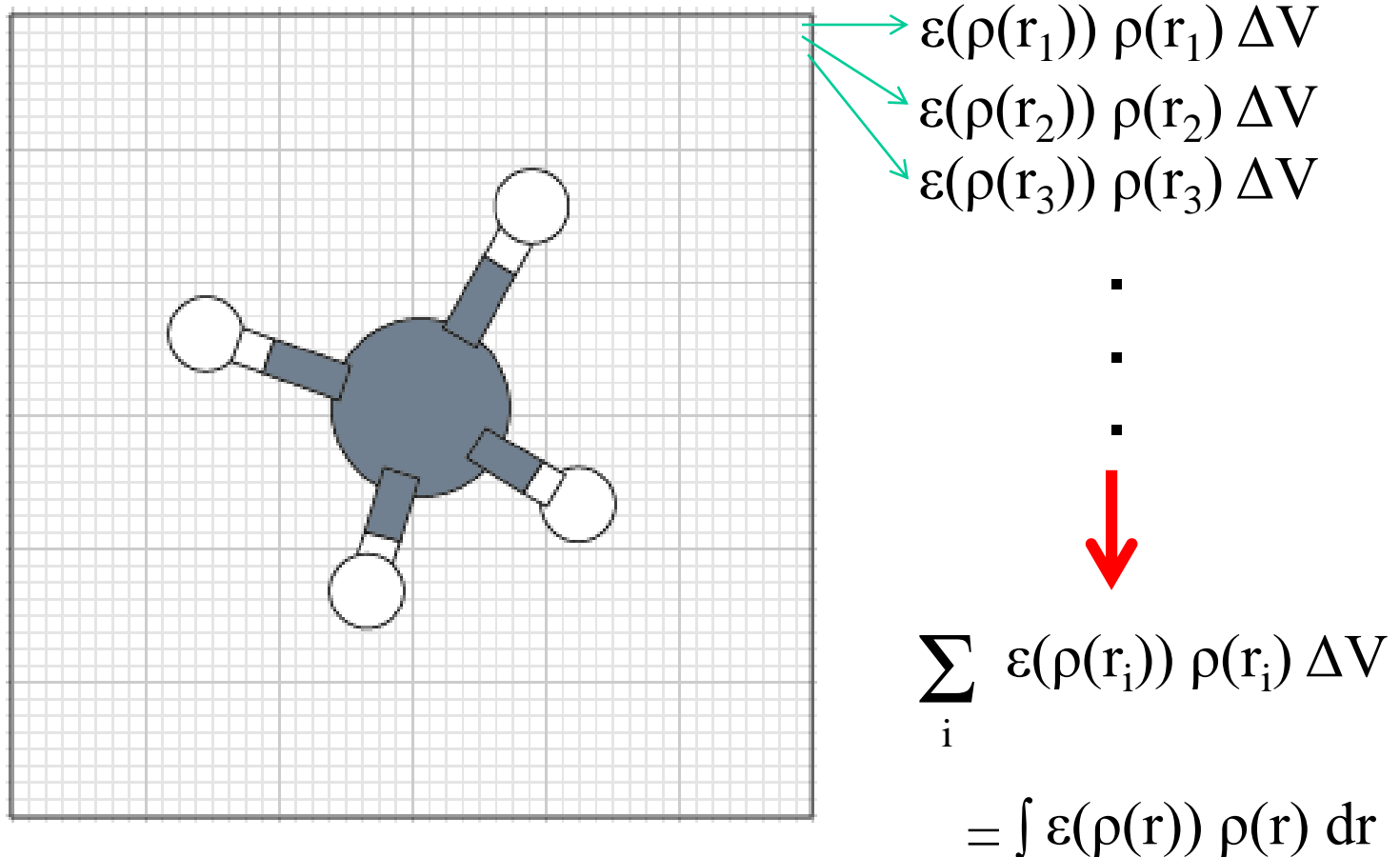
Exchange energy

$$\frac{E_1}{N} = -\frac{3e^2}{4}\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}$$

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 ρ.

$\varepsilon(\rho(r_1))\, \rho(r_1)\, \Delta V$

$\varepsilon(\rho(r_2))\, \rho(r_2)\, \Delta V$

$\varepsilon(\rho(r_3))\, \rho(r_3)\, \Delta V$

.
.
.

$$\sum_i \varepsilon(\rho(r_i))\, \rho(r_i)\, \Delta V$$

$$= \int \varepsilon(\rho(r))\, \rho(r)\, dr$$

Thomas-Fermi model: The simplest density functional

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

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

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

The kinetic energy density t(ρ) is that of non-interacting electrons in the jellium model.

The second quantized Hamiltonian of the jellium model

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

$$\begin{aligned}
\frac{E^{(0)}}{N} &= \frac{1}{N} \langle F | \hat{H}_0 | F \rangle \\
&= \frac{1}{2N} \sum_{\mathbf{k}\lambda} k^2 \langle F | \hat{n}_{\mathbf{k}\lambda} | F \rangle \\
&= \frac{1}{2N} \sum_{\mathbf{k}\lambda} k^2 \theta(k_F - k) \\
&= \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \rho^{\frac{2}{3}}
\end{aligned}$$

Thomas-Fermi-Dirac model
LDA to the kinetic and exchange, but no correlation

$$E_{\mathrm{TFD}} = \int \rho(\mathbf{r})t(\rho)d\mathbf{r} + \boxed{\int \rho(\mathbf{r})\varepsilon_{\mathrm{x}}(\rho)d\mathbf{r}} + \int \rho(\mathbf{r})v_{\mathrm{ext}}d\mathbf{r} + \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2 + \sum_{I,J}\frac{Z_I Z_J}{|\mathbf{R}_1 - \mathbf{R}_2|}$$

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

The first order perturbation energy in the jellium model is used as the exchange energy density $\varepsilon_{\mathrm{x}}(\rho)$.
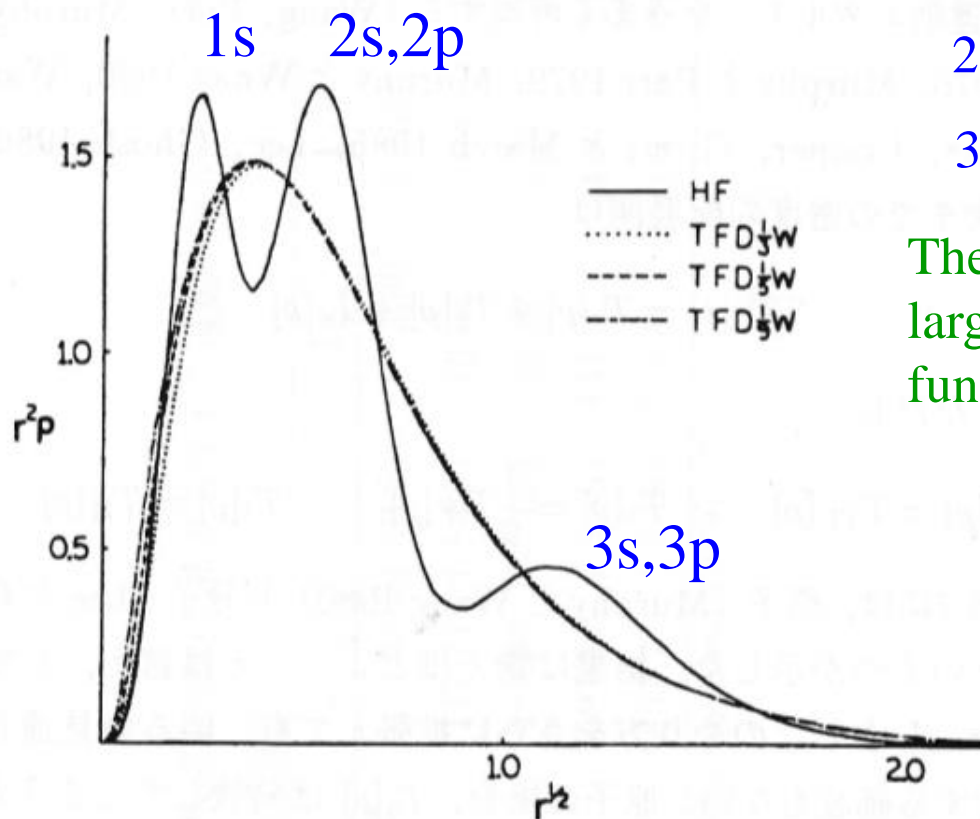
The second quantized Hamiltonian of the jellium model

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

$$
\begin{aligned}
\frac{E^{(1)}}{N} &= \frac{1}{N}\langle F|\hat{H}_1|F\rangle \\
&= \frac{1}{2NV}\sum_{\mathbf{kpq}}'\sum_{\lambda_1\lambda_2}\frac{4\pi}{q^2}\langle F|a_{\mathbf{k}+\mathbf{q},\lambda_1}^{\dagger}a_{\mathbf{p}-\mathbf{q},\lambda_2}^{\dagger}a_{\mathbf{p}\lambda_2}a_{\mathbf{k}\lambda_1}|F\rangle \\
&= -\frac{1}{2NV}\sum_{\lambda_1}\sum_{\mathbf{kq}}'\frac{4\pi}{q^2}\theta(k_F - |\mathbf{k}+\mathbf{q}|)\theta(k_F - k|) \\
&= \boxed{-\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{1}{3}}}
\end{aligned}
$$

Failures of Thomas-Fermi-Dirac model

Electron density of Ar

1s   2s,2p

by W.Yang, 1986

1. No shell structure of atoms

2. No binding of atoms

3. 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.)

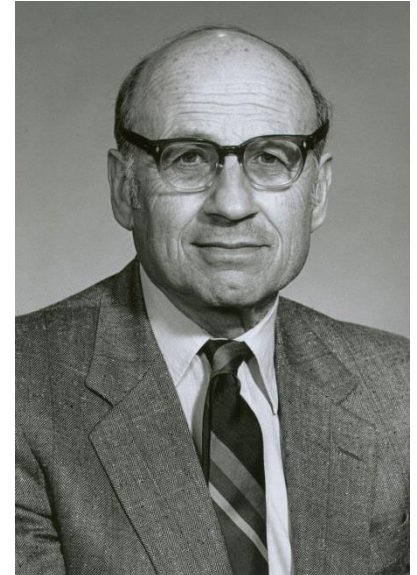|	
HF[a]	526.82
TF[b]	489.95
KS-LDA	525.95

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.

$$E[\rho] = \int \rho(\mathbf{r})v(\mathbf{r})d + T[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho]$$

$$F_{\mathrm{HK}}[\rho]$$

W.Kohn (1923-)

The second theorem

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 ρ.

$$\hat{H} = \hat{T} + v \longrightarrow \hat{H}\Psi = E\Psi$$
$$\hat{H}' = \hat{T} + v' \longrightarrow \hat{H}'\Psi' = E'\Psi'$$
$$\searrow \rho$$

$$
\begin{aligned}
E < \langle\Psi'|\hat{H}|\Psi'\rangle &= \langle\Psi'|\hat{H}'|\Psi'\rangle + \langle\Psi'|(\hat{H} - \hat{H}')|\Psi'\rangle \\
&= E' + \int \rho(\mathbf{r})(v(\mathbf{r}) - v'(\mathbf{r}))d\mathbf{r} \\
E' < \langle\Psi|\hat{H}'|\Psi\rangle &= \langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi|(\hat{H}' - \hat{H})|\Psi\rangle \\
&= E - \int \rho(\mathbf{r})(v(\mathbf{r}) - v'(\mathbf{r}))d\mathbf{r}
\end{aligned}
$$

Adding above two equations leads to

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

A discrepancy occurs. Thus, for a given v, ρ is uniquely determined.

It was assumed the v-representability that a corresponding v exists for a given ρ.
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,

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

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

$$v \longrightarrow \rho \quad \cdots \quad (A)$$

but never show

$$v \longleftarrow \rho \quad \cdots \quad (B)$$

If the condition (B) is satisfied for a given ρ, it is mentioned that the density ρ 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 ρ, it is mentioned that the density ρ is N-representable.

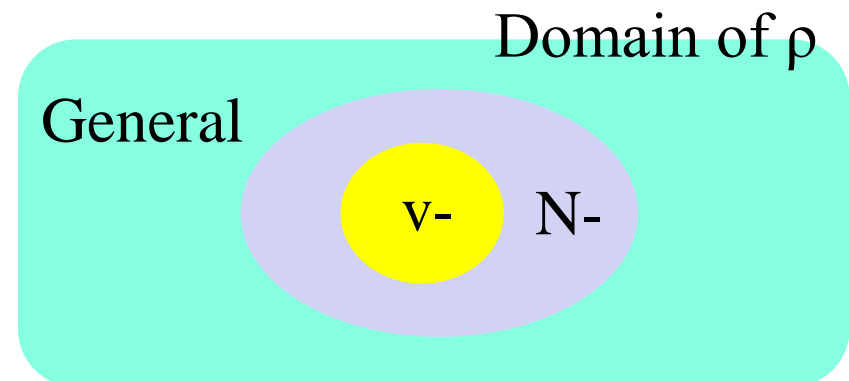$$\Psi \longleftarrow \rho \quad \cdots \quad (C)$$

v-representability
$$v \Leftrightarrow \Psi \Leftrightarrow \rho$$

N-representability
$$v \overset{?}{\Leftrightarrow} \Psi \Leftrightarrow \rho$$

General case
$$v \overset{?}{\Leftrightarrow} \Psi \overset{?}{\Leftrightarrow} \rho$$

Domain of ρ

General

v-   N-

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

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

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 ρ_{GS}.

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

Proof of the theorem by Levy

Let us consider a constraint minimization of E.

$$
\begin{aligned}
E_{\mathrm{GS}} &= \min_{\Psi} \langle \Psi | (\hat{T} + \hat{V}_{\mathrm{ee}} + v_{\mathrm{ext}}) | \Psi \rangle \\
&= \min_{\rho} \left\{ \min_{\Psi \to \rho} \langle \Psi | (\hat{T} + \hat{V}_{\mathrm{ee}} + v_{\mathrm{ext}}) | \Psi \rangle \right\} \\
&= \min_{\rho} \left\{ \min_{\Psi \to \rho} \langle \Psi | (\hat{T} + \hat{V}_{\mathrm{ee}}) | \Psi \rangle + \int v_{\mathrm{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\} \\
&= \min_{\rho} \left\{ F[\rho] + \int v_{\mathrm{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\}
\end{aligned}
$$

The first line is just a conventional variational problem with respect to ψ.

In the second line, two step minimization is introduced.
  (1) Choose N-representable ρ
  (2) Minimize E with respect to ψ giving ρ $\min_{\Psi \to \rho}$
  (3) Repeat steps (1), (2) $\min_{\rho}$

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 ρ_{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.

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

The kinetic energy of non-interacting electrons

$$
T_s = -\frac{1}{2} \sum_{i=1}^{\text{occ}} \int \phi_i \nabla^2 \phi_i d\mathbf{r}
$$

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 funtions.

$$
\frac{\delta E}{\delta \phi} = 0
$$

$$
\boxed{
\begin{aligned}
\hat{H}_{\text{KS}} \phi_i &= \varepsilon_i \phi_i \\
\hat{H}_{\text{KS}} &= -\frac{1}{2} \nabla^2 + v_{\text{eff}}
\end{aligned}
}
$$

KS effective potential

$$
v_{\text{eff}} = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}
$$

$$
v_{\text{Hartree}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'
$$

Comparison of the kinetic energy of Ar

HF[a]	526.82
TF[b]	489.95
KS-LDA	525.95

in a.u.

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

Proof of $\dfrac{\delta E}{\delta \rho} = 0$

KS eq. is derived by assuming δE/δφ=0.
However, how about δE/δρ=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.

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

To satisfy δE=0 for arbitrary δρ, 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, ρ calculated by the KS eq. satisfies δE/δρ=0, which might be the density of the ground state.

Eigenvalue of KS eq.

The physical meaning of eigenvalues ε is non-trivial, since ε 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 ε_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

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

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

Semiconducting SWCNT

Metallic SWCNTs

SWNT (14,3)

Theory, 6-31G* (b)

pbe0

pbe

STS Experiment

(a)

DOS, arb. units

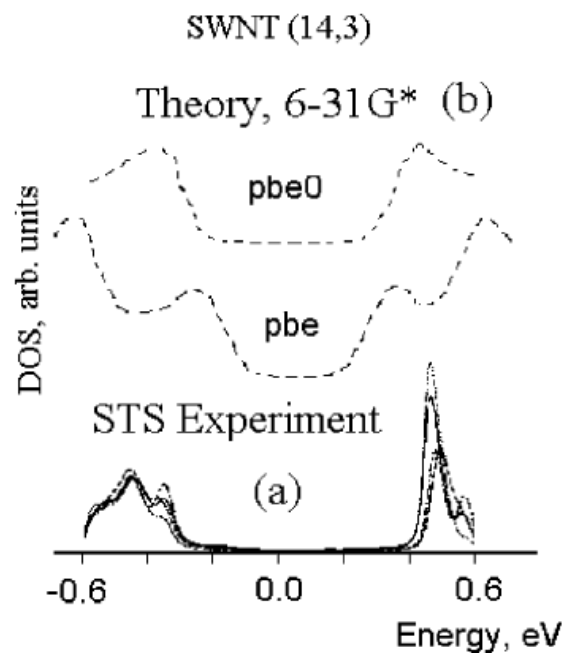-0.6   0.0   0.6

Energy, eV

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.

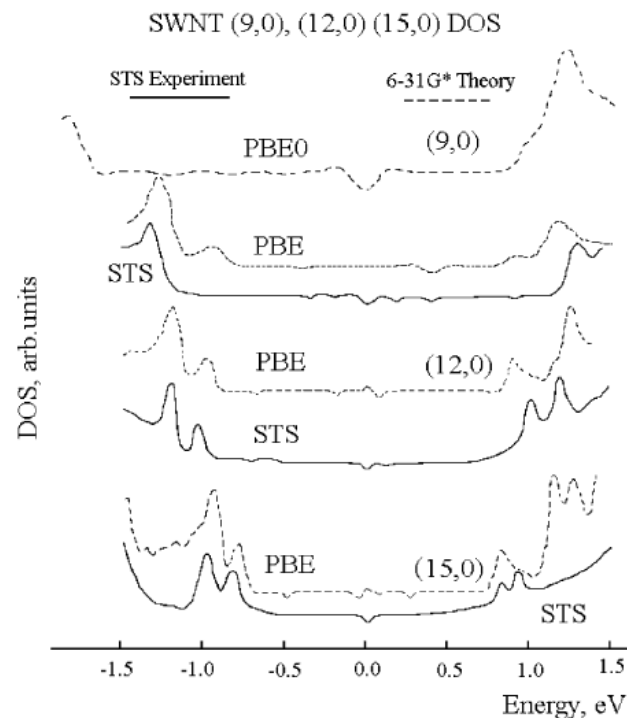SWNT (9,0), (12,0) (15,0) DOS

STS Experiment   6-31G* Theory

PBE0   (9,0)

PBE

STS

PBE   (12,0)

STS

PBE   (15,0)

STS

DOS, arb. units

-1.5   -1.0   -0.5   0.0   0.5   1.0   1.5

Energy, eV

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.

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.
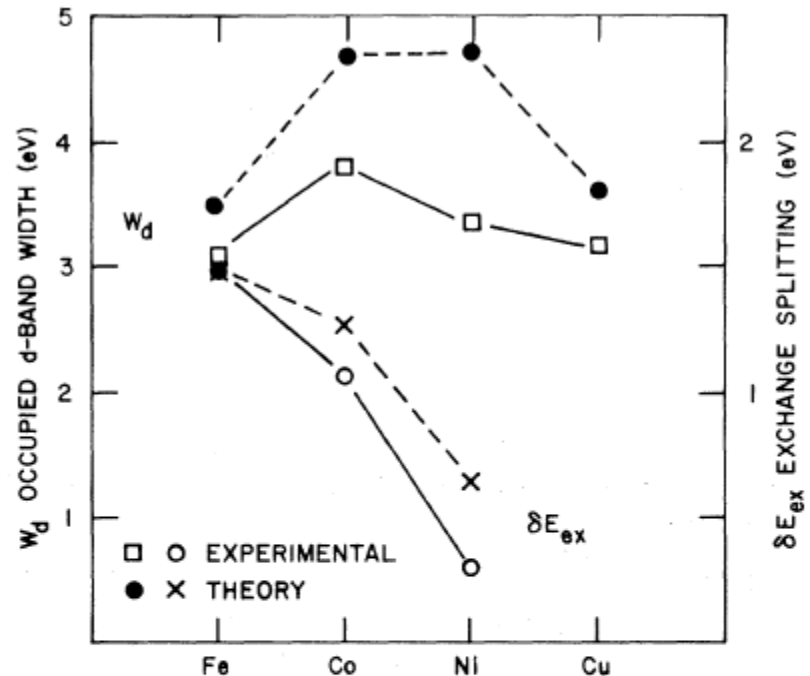

FIG. 4. Occupied d-band widths (eV) and magnetic exchange splittings (293 K). The widths are at the symmetry points P, L, L, and X, and at X for Fe, Co, Ni, and Cu, respectively, while the exchange splittings are at P, Γ, and near L for Fe, Co, and Ni, respectively. Theoretical widths are taken from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

Approximation to E_{xc}

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

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

ε_{xc} is an exchange-correlation energy density of jellium model with the electron density ρ.

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 evaluated 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)

$$\varepsilon_c = A\left\{\ln\frac{x^2}{X(x)} + \frac{2b}{Q}\tan^{-1}\frac{Q}{2x+b} - \frac{bx_0}{X(x_0)}\left[\ln\frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q}\tan^{-1}\frac{Q}{2x+b}\right]\right\}$$

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

$$x = r_s^{1/2}$$

$$Q = (4c - b^2)^{1/2}$$
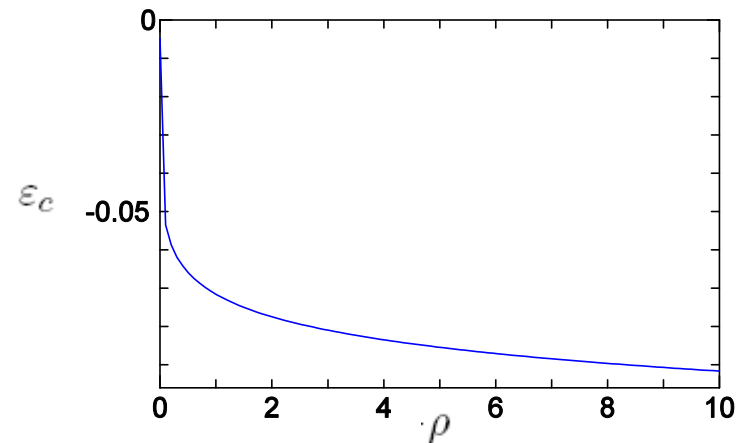
$$X(x) = x^2 + bx + c$$

$A = 0.0310907$

$b = 3.72744$

$c = 12.9352$

$x_0 = -0.10498$

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

$$\nabla \rho(\mathbf{r}) \frac{2\pi}{k_{\mathrm{F}}(\mathbf{r})} << \rho(\mathbf{r}) \qquad \cdots (A)$$

with $k_{\mathrm{F}}(\mathbf{r}) = \{3\pi^2 \rho(\mathbf{r})\}^{1/3}$ 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.
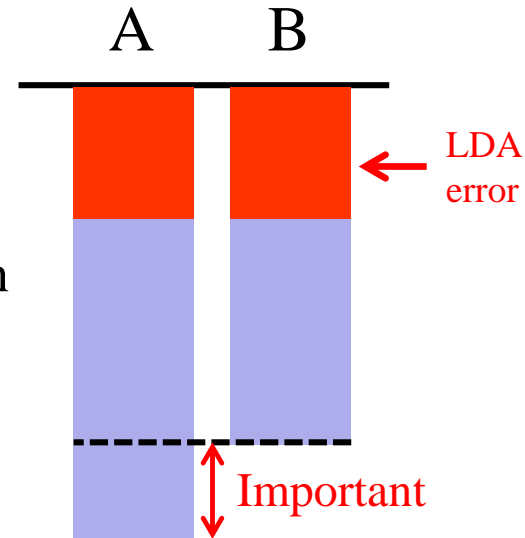
1. Sum rule in the xc hole density

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.

Exchange-correlation hole

Exchange energy

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

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

Correlation energy

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

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

An important consequence is that only the spherical average of exchange-correlation hole can attribute to the xc energy.
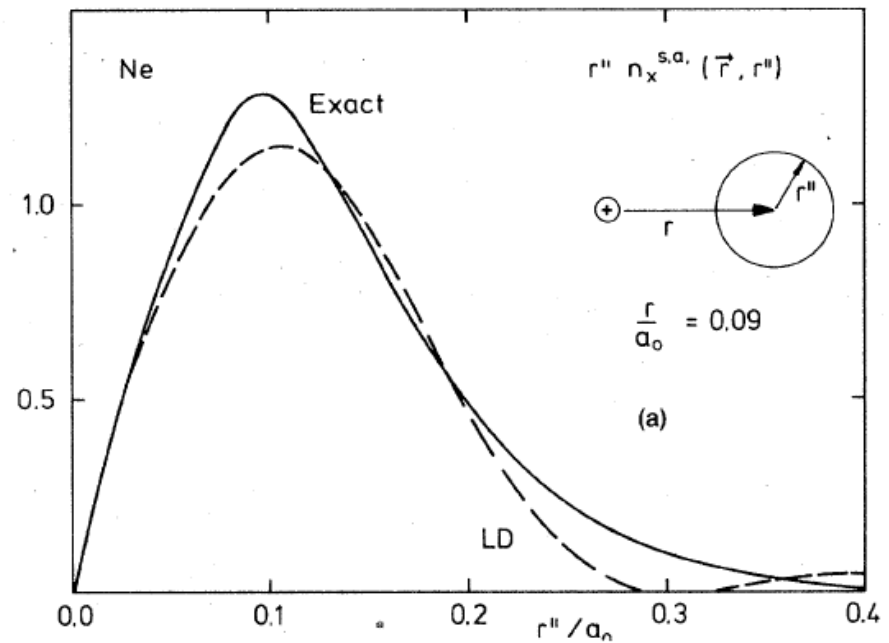
$$E_{\mathrm{xc}} = \frac{1}{2} \int d\mathbf{r}\rho(\mathbf{r}) \int_0^\infty 4\pi s ds \rho_{\mathrm{xc}}^{\mathrm{SA}}(\mathbf{r}, s)$$

Exchange hole of Ne and its spherical average

Exchange hole

Its spherical average

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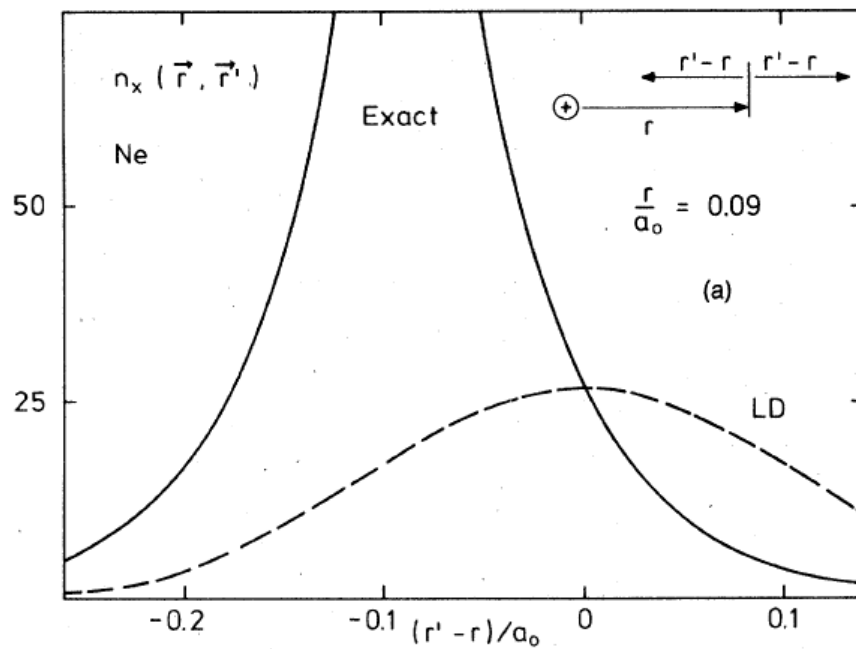
Deficiencies of LDA

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: structure 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)

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 → 0.

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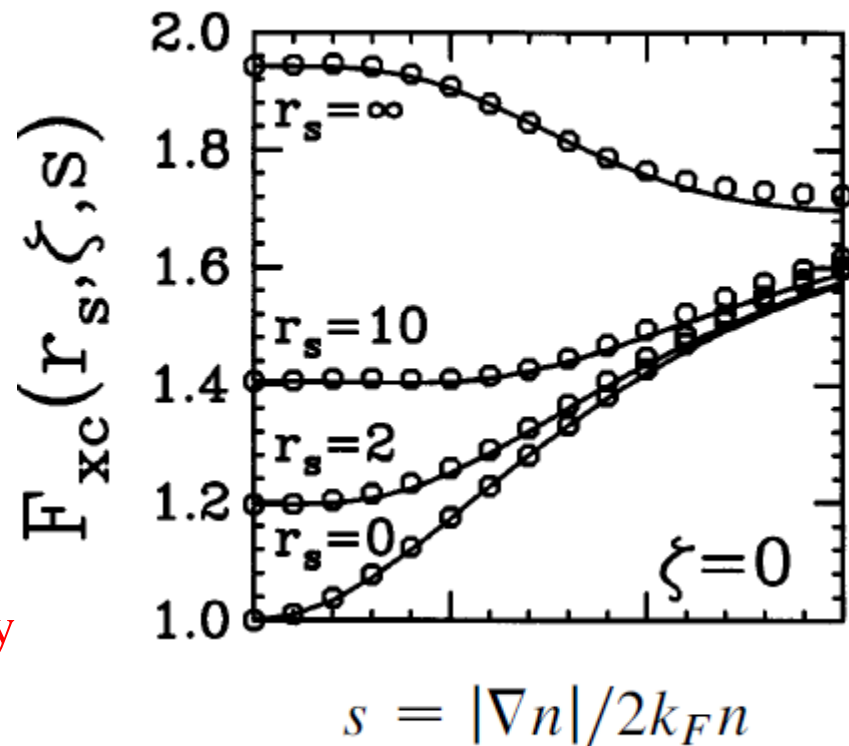
$\epsilon_X^{unif} = -3e^2 k_F/4\pi$ < 0

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

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

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

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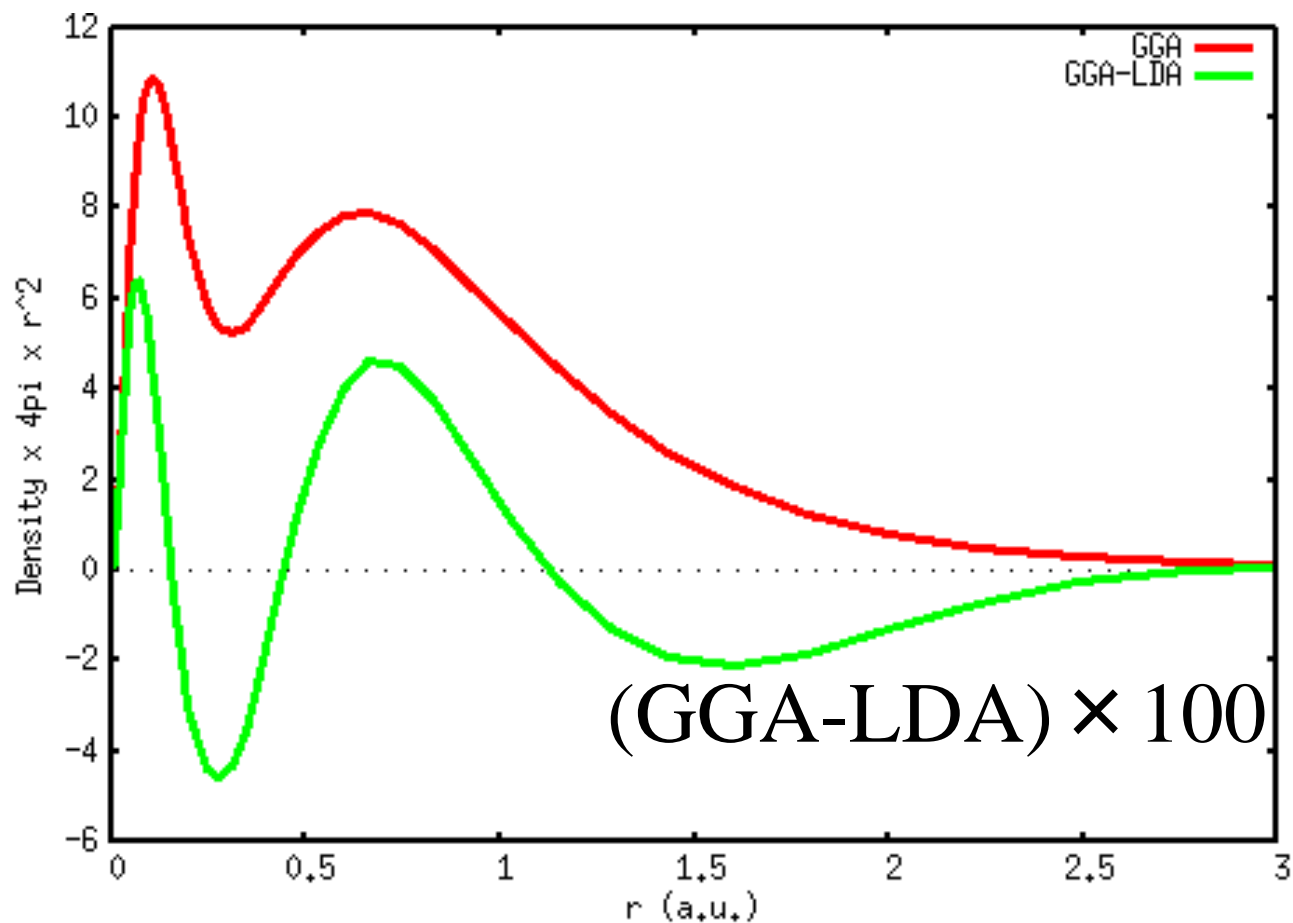
For most physical r_s, GGA favors density inhomogeneity more than LDA does.

LDA vs GGA: ρ of Ne

At two shell structures, GGA favors more localized states.
GGA favors density inhomogeneity→ localized states are favored.

(GGA-LDA) × 100

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
H	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.
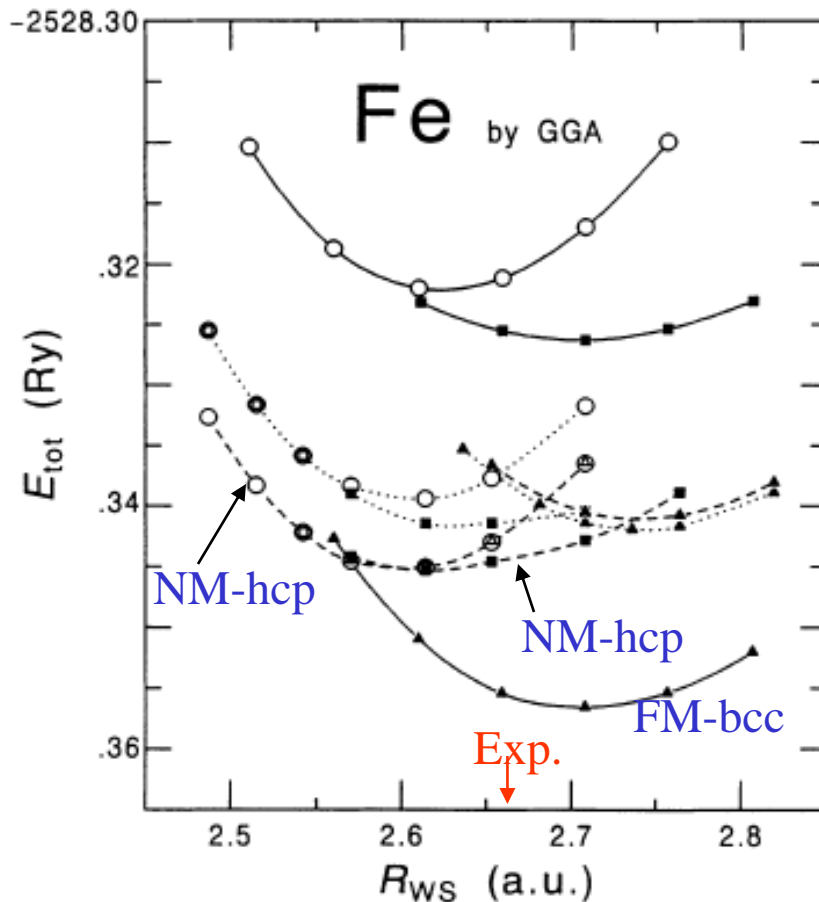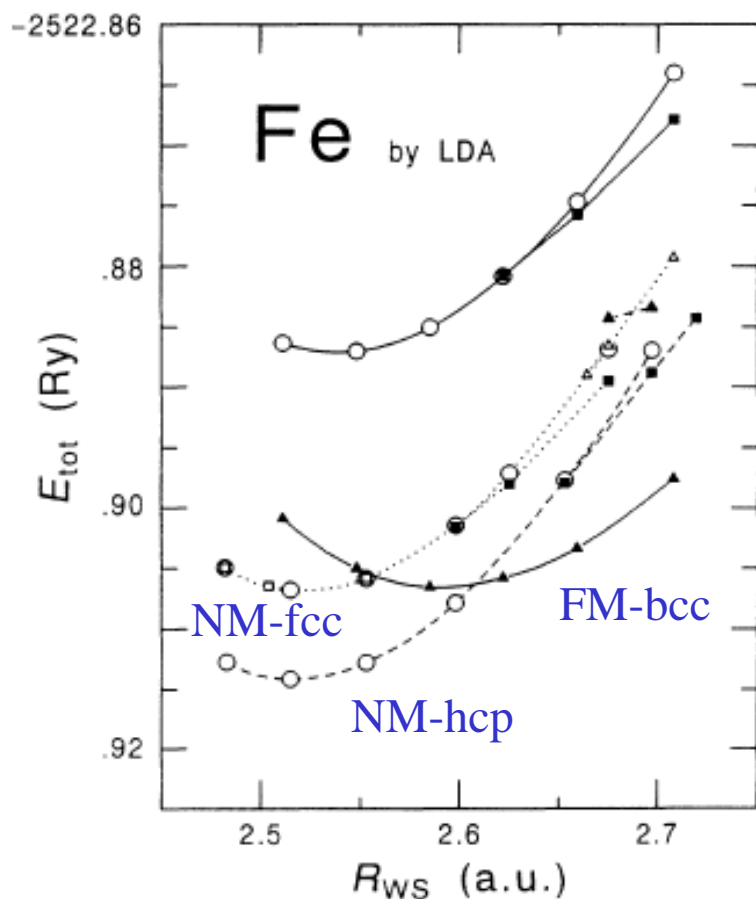
Comparison between LDA and GGA: Structural properties of bulks

Solid	a_0				B_0			
	LDA	PBE	WC	Expt.[a]	LDA	PBE	WC	Expt.[a]
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
Cu (A1)	*3.522*	**3.632**	3.573	3.615	*191*	**141**	168	133
Ge (A4)	**5.632**	5.769	5.686	5.652	**72.7**	59.5	67.8	75.8
Rb (A2)	*5.374*	5.670	**5.609**	5.59	3.59	**2.77**	2.71	3.06
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

F. Tran et al., PRB 75, 115131 (2007).

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

Successes and failures of GGA

Successes:

1. Accuracy:

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

2. Accurate description of hydrogen bonding

3. Better description of magnetic ground states (e.g., bcc Fe)

Failures:

1. Band gap:	Underestimation of 30 %
2. vdW interaction:	No binding in many cases
3. Strongly correlation:	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.
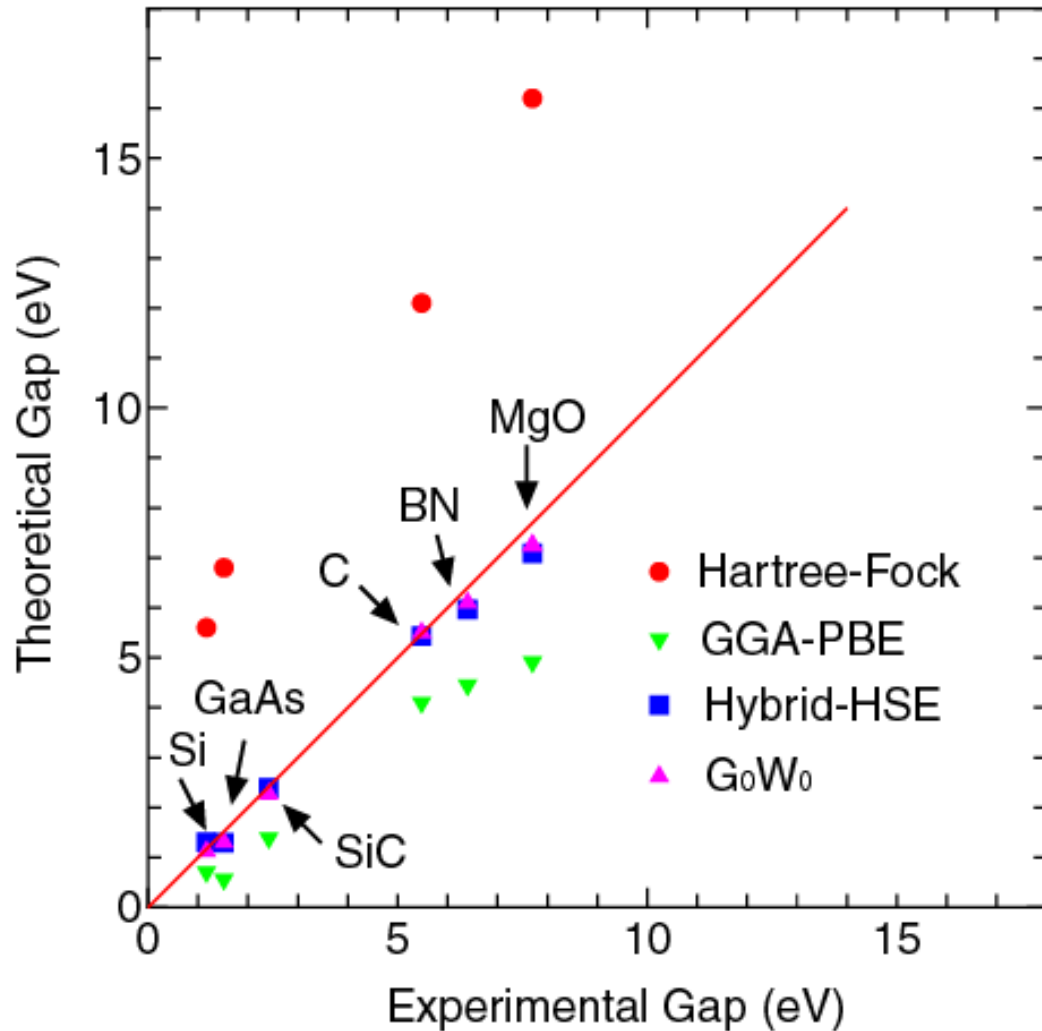
2. Orbital dependent functional (DFT+U method)

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

Hartree-Fock

Multi-configurational Hatree-Fock

GGA

$$\Psi = c_1\varphi_1 + c_2\varphi_2 + \ldots$$

V_{eff} consisting of N

V_{eff} consisting of N-1

V_{eff} consisting of N
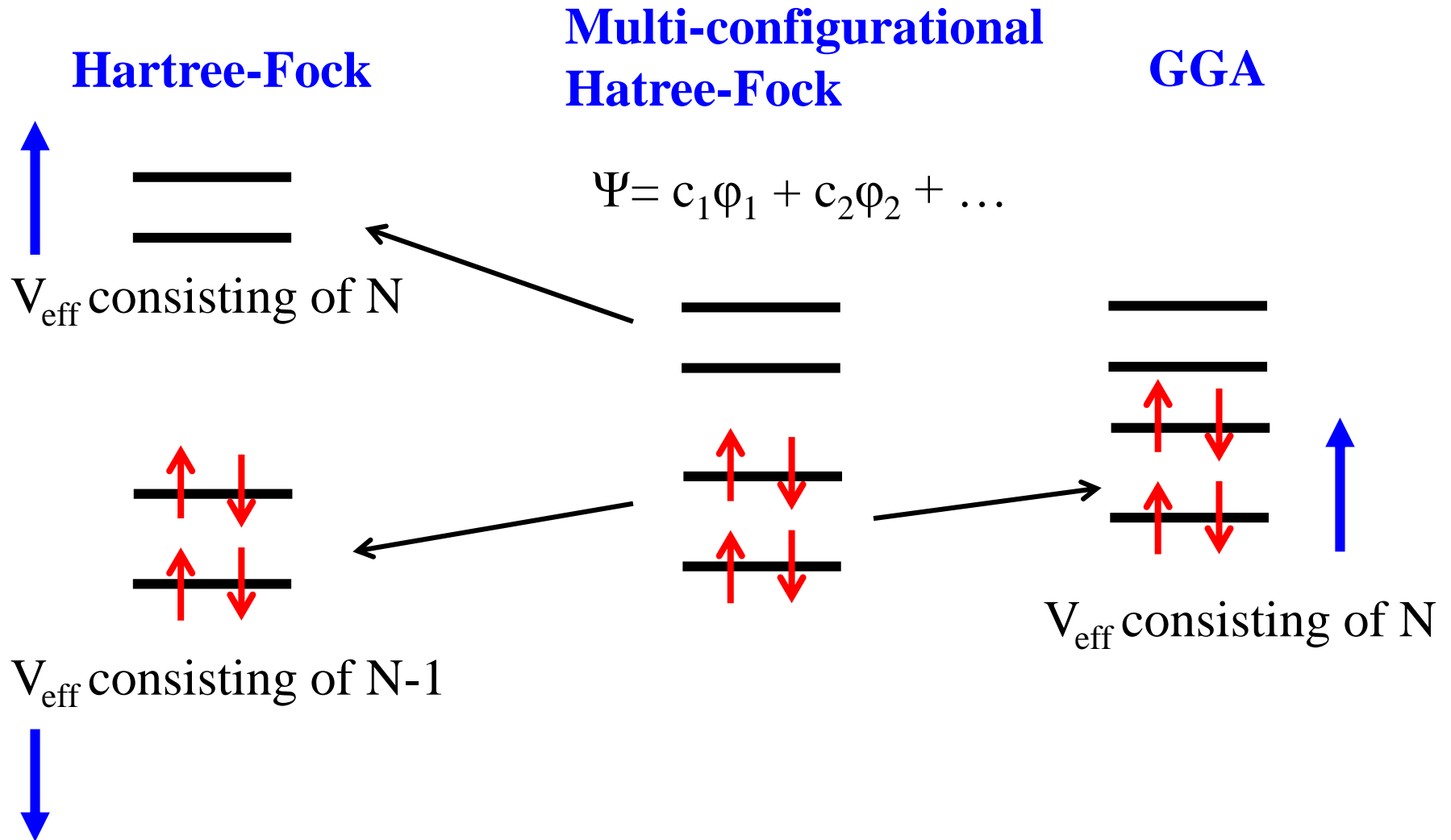
Band gap by a hybrid functional

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.

$$E_c^{nl}[n] = \int d^3r \int d^3r' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}').$$

Dion et al., PRL 92, 246401 (2004).
Lee et al., PRB 82, 081101(R) (2010).
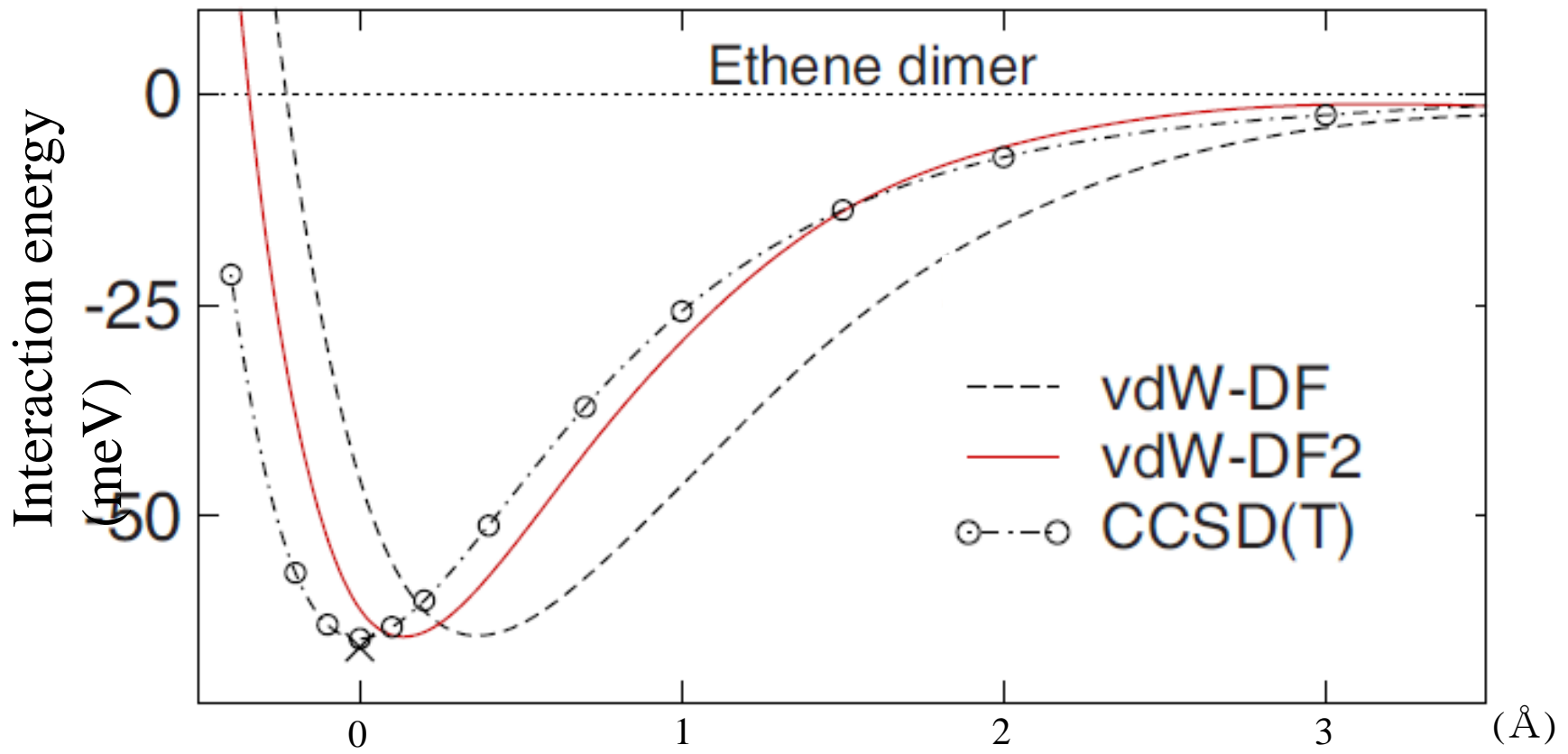
General consideration of Self-interaction and orbital polarization

Consider degenerate states are partially filled e.g., d-orbitals 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 self-interaction.

If there is no spurious interaction, a naive consideration implies that the left case leads to interaction of 4/3(=3*2/3*2/3), while in right case the interaction of 1(=1*1*1).
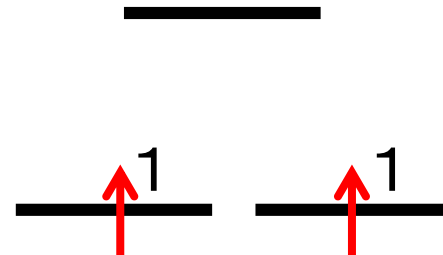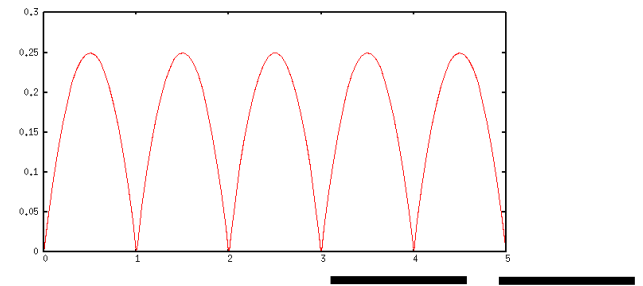
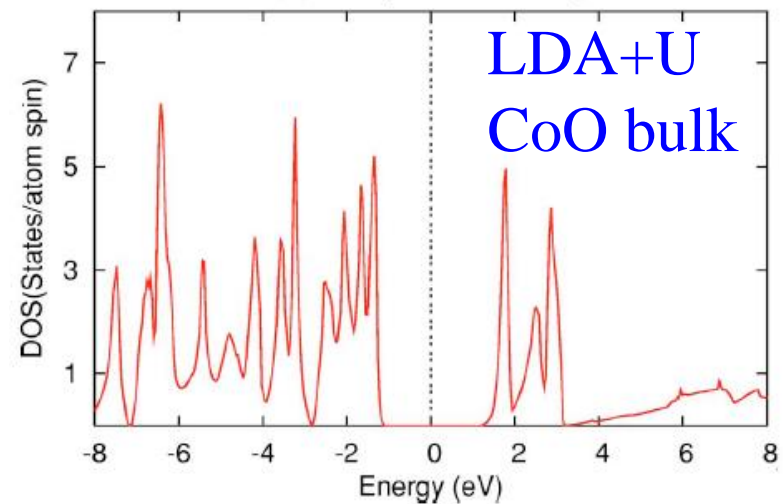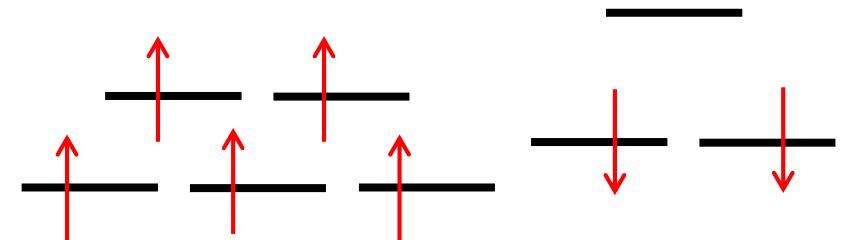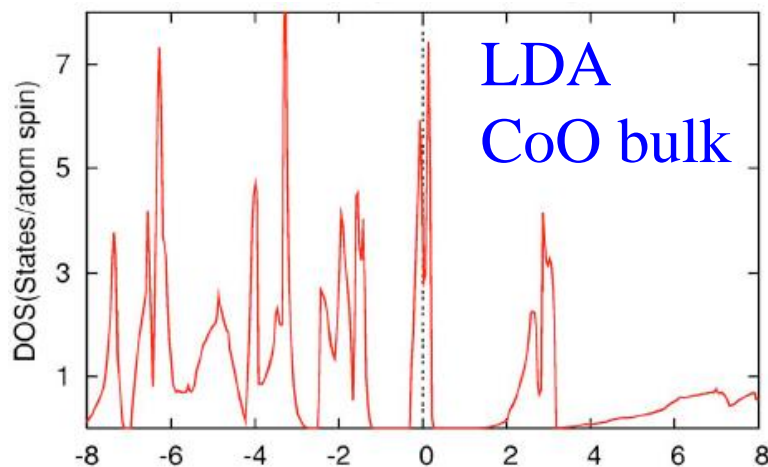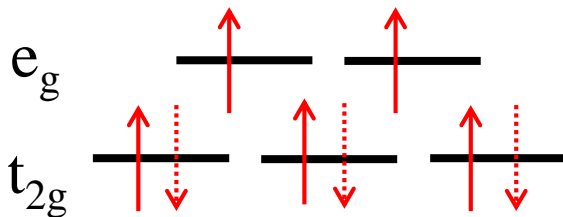# Orbital polarization of localized d-electrons: Importance of orbital dependent functional

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

Han et al., PRB 73, 045110 (2006).

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

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

LDA
CoO bulk

LDA+U
CoO bulk

Outlook

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