Notes on Hohenberg-Kohn theorem and Kohn-Sham method

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Slater's $X\alpha$ method   Phys. Rev. 81, 385 (1951)

Slater considered to simplify the Hartree-Fock method.

Let us start our discussion by writting the exchange energy:

$$E_x = \frac{1}{2}\sum_{\ell=1}^{N}\sum_{\ell'=1}^{N}\left(-\iint dx\,dx'\,\varphi_\ell^*(x)\,\varphi_{\ell'}(x')\frac{1}{|x-x'|}\varphi_\ell(x')\,\varphi_{\ell'}(x')\right) \quad \cdots\cdots (1)$$

Remembering $\varphi(x) = \phi(\mathbf{r})\eta(\sigma)$, and

$$\iint dx\,dx'\,\varphi_\ell^*(x)\,\varphi_{\ell'}(x')\frac{1}{|x-x'|}\varphi_\ell(x')\,\varphi_{\ell'}(x')$$

$$= \int d\sigma_1\,\eta^*(\sigma_1)\,\eta'(\sigma_1)\int d\sigma_2\,\eta(\sigma_2)\,\eta'^*(\sigma_2)\iint d\mathbf{r}^3 d\mathbf{r}'^3\,\phi_\ell^*(\mathbf{r})\phi_{\ell'}(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_\ell(\mathbf{r}')\,\phi_{\ell'}^*(\mathbf{r}')$$

$$= \delta_{\eta\eta'}\iint d\mathbf{r}^3 d\mathbf{r}'^3\,\phi_\ell^*(\mathbf{r})\phi_{\ell'}(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_\ell(\mathbf{r}')\,\phi_{\ell'}(\mathbf{r}') \quad \cdots\cdots (2)$$

Changing the variables as $\ell \to i\sigma$, $\ell' \to i\sigma'$, we can write as

$$E_x = -\frac{1}{2}\sum_\sigma\sum_i\sum_j\iint d\mathbf{r}^3 d\mathbf{r}'^3\,\phi_{i\sigma}^*(\mathbf{r})\phi_{j\sigma}^*(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{j\sigma}(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}') \quad \cdots\cdots (3)$$

By introducing the exchange hole density $\rho_x^\sigma(\mathbf{r},\mathbf{r}')$,

$$\rho_x^\sigma(\mathbf{r},\mathbf{r}') = -\frac{\left|\sum_i^{occ.}\phi_{i\sigma}^*(\mathbf{r})\,\phi_{i\sigma}(\mathbf{r}')\right|^2}{\rho^\sigma(\mathbf{r})} \quad \cdots\cdots (4)$$

E_x of Eq. (3) can be rewritten as

$$E_x = \frac{1}{2}\sum_\sigma\int d\mathbf{r}^3\int d\mathbf{r}'^3\,\frac{\rho^\sigma(\mathbf{r})\,\rho_x^\sigma(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \cdots\cdots (5)$$

From Eq. (5) E_x can be understood by a Coulombic interaction between the electron density and the exchange hole.

The exchange hole density ρ_x^σ of Eq.(4) can be transformed as

$$\rho_x^\sigma(\mathbf{r},\mathbf{r}') = -\frac{\left|\sum_i^{occ}\phi_{i\sigma}^*(\mathbf{r})\,\phi_{i\sigma}(\mathbf{r}')\right|^2}{\rho^\sigma(\mathbf{r})}$$

$$= -\frac{1}{\rho^\sigma(\mathbf{r})}\left(\sum_j^{occ}\phi_{j\sigma}(\mathbf{r})\,\phi_{j\sigma}^*(\mathbf{r}')\right)\left(\sum_i^{occ}\phi_{i\sigma}^*(\mathbf{r})\,\phi_{i\sigma}(\mathbf{r}')\right)$$

$$= \sum_i^{occ}\frac{|\phi_{i\sigma}(\mathbf{r})|^2}{\rho^\sigma(\mathbf{r})}\left(-\frac{\phi_{i\sigma}^*(\mathbf{r})\,\phi_{i\sigma}(\mathbf{r}')\sum_j^{occ}\phi_{j\sigma}(\mathbf{r})\,\phi_{j\sigma}^*(\mathbf{r}')}{|\phi_{i\sigma}(\mathbf{r})|^2}\right)$$

where we introduce

$$w_i^\sigma(\mathbf{r}) = \frac{|\phi_{i\sigma}(\mathbf{r})|^2}{\rho^\sigma(\mathbf{r})} \quad \cdots\cdots (6)$$

$$\gamma_x^{i\sigma}(\mathbf{r},\mathbf{r}') = -\frac{\phi_{i\sigma}^*(\mathbf{r})\,\phi_{i\sigma}(\mathbf{r}')\sum_j^{occ}\phi_{j\sigma}(\mathbf{r})\,\phi_{j\sigma}^*(\mathbf{r}')}{|\phi_{i\sigma}(\mathbf{r})|^2} \quad \cdots (7)$$

$$\rho_x^\sigma(\mathbf{r},\mathbf{r}') = \sum_i^{occ} w_i^\sigma(\mathbf{r})\,\gamma_x^{i\sigma}(\mathbf{r},\mathbf{r}') \quad \cdots\cdots (8)$$

For ρ_x^σ and $\gamma_x^{i\sigma}$, we have the following properties:

$$\rho_x^\sigma(\mathbf{r},\mathbf{r}) = -\rho^\sigma(\mathbf{r}), \quad \int dr'^3\,\rho_x^\sigma(\mathbf{r},\mathbf{r}') = -1$$

$$\gamma_x^{i\sigma}(\mathbf{r},\mathbf{r}) = -\rho^\sigma(\mathbf{r}), \quad \int dr'^3\,\gamma_x^{i\sigma}(\mathbf{r},\mathbf{r}') = -1 \quad \cdots\cdots (9)$$

From Eq.(8), we have a view that the exchange hole density ρ_x^σ is given by a weighted sum of $\gamma_x^{i\sigma}$ with the weight of w_i^σ.

Now we consider the Hartree-Fock equation:

$$\hat{V}_1(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) + \left[\sum_j^{occ}\int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi^*_{j\sigma}(\mathbf{r}')\phi_{j\sigma}(\mathbf{r}')\right]\phi_{i\sigma}(\mathbf{r}) \quad \cdots\cdots (10)$$

$$-\left[\sum_j^{occ}\int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{i\sigma}(\mathbf{r}')\phi^*_{j\sigma}(\mathbf{r}')\right]\phi_{j\sigma}(\mathbf{r}) = \varepsilon_i\,\phi_{i\sigma}(\mathbf{r})$$

The last term of the left-hand side can be transformed as

$$-\left[\sum_j^{occ}\int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{i\sigma}(\mathbf{r}')\phi^*_{j\sigma}(\mathbf{r}')\right]\phi_{j\sigma}(\mathbf{r})$$

$$= \left[\int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left(-\frac{\phi^*_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}')\sum_j^{occ}\phi^*_{j\sigma}(\mathbf{r}')\phi_{j\sigma}(\mathbf{r})}{|\phi_{i\sigma}(\mathbf{r})|^2}\right)\right]\phi_{i\sigma}(\mathbf{r})$$

$$= \left[\int d\mathbf{r}'^3 \frac{1}{|\mathbf{r}-\mathbf{r}'|}\gamma_x^{i\sigma}(\mathbf{r},\mathbf{r}')\right]\phi_{i\sigma}(\mathbf{r}) \qquad V_x^{i\sigma} = \int d\mathbf{r}'^3 \frac{\gamma_x^{i\sigma}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \cdots (11)$$

$$= V_x^{i\sigma}(\mathbf{r})\,\phi_{i\sigma}(\mathbf{r}) \quad \cdots\cdots (12)$$

$V_x^{i\sigma}$ is called the exchange potential which depends on the state $i\sigma$ for which $V_x^{i\sigma}$ is applied.

To eliminate the dependency of $V_x^{i\sigma}$ on the state i, Slater introduced an approximation:

$$V_x^{\sigma}(\mathbf{r}) = \sum_i^{occ.} W_i^{\sigma}(\mathbf{r})\,V_x^{i\sigma}(\mathbf{r}) \quad \cdots\cdots (13)$$

$$= \sum_i \frac{|\phi_{i\sigma}(\mathbf{r})|^2}{\rho^{\sigma}(\mathbf{r})} \times \int d\mathbf{r}'^3 \frac{1}{|\mathbf{r}-\mathbf{r}'|}\gamma_x^{i\sigma}(\mathbf{r},\mathbf{r}')$$

$$= \sum_i \left(\frac{|\phi_{i\sigma}(\mathbf{r})|^2}{\rho^{\sigma}(\mathbf{r})}\int d\mathbf{r}'^3 \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left(-\frac{\phi^*_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}')\sum_j\phi^*_{j\sigma}(\mathbf{r}')\phi_{j\sigma}(\mathbf{r})}{|\phi_{i\sigma}(\mathbf{r})|^2}\right)\right)$$

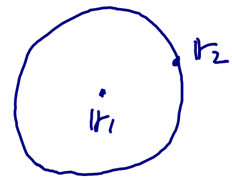
$$= \int d\mathbf{r}'^3\left(-\frac{|\sum_i\phi^*_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}')|^2}{\rho^{\sigma}(\mathbf{r})}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right) = \int d\mathbf{r}'^3 \frac{\rho_x^{\sigma}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \cdots (14)$$

To evaluate Eq. (14), Slater further approximated ρ_x^σ using the result of jellium model as

$$\rho_\sigma^x(\mathbf{r}_1, \mathbf{r}_2) = -\frac{9}{2}\rho(\mathbf{r})\left\{\frac{j_1(k_F r_{12})}{k_F r_{12}}\right\}^2 \quad \cdots\cdots (15)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$

Then, we have



$$V_x^\sigma(\mathbf{r}) = V_x^\sigma(\mathbf{r}_1) = \int d\mathbf{r}_2^3 \frac{\rho_x^\sigma(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$= -\frac{9}{2}\rho(\mathbf{r})\int d\mathbf{r}_2^3 \left\{\frac{j_1(k_F r_{12})}{k_F r_{12}}\right\}^2 \frac{1}{r_{12}}$$

$$= -\frac{9}{2}\rho(\mathbf{r}) \times 4\pi \int_0^\infty dr \cdot r^2 \frac{1}{k_F^2 r^3} \times (j_1(k_F r))^2$$

$$\left(x = k_F r \rightarrow dr = \frac{1}{k_F}dx, \quad \rho(\mathbf{r}) = \frac{k_F^3}{3\pi^2}, \right.$$

$$= -18\pi \times \frac{k_F^3}{3\pi^2} \times \frac{1}{k_F^2}\int_0^\infty dx \frac{1}{x}(j_1(x))^2$$

$$= -\frac{6}{\pi}k_F \int_0^\infty dx \frac{1}{x}(j_1(x))^2 = -\frac{6}{\pi}k_F \times \frac{1}{4}$$

Thus,

$$V_x^\sigma(\mathbf{r}) = -\frac{3}{2\pi}k_F = -\frac{3}{2\pi}(3\pi^2 \times 2\rho^\sigma)^{\frac{1}{3}}$$

$$= -3\left(\frac{6\pi^2\rho^\sigma}{8\pi^3}\right)^{\frac{1}{3}} = -3\left(\frac{3\rho^\sigma}{4\pi}\right)^{\frac{1}{3}} \quad \cdots\cdots (16)$$

By introducing a parameter α, we have

Slater's $X\alpha$ potential:

$$\boxed{V_x^\sigma(\mathbf{r}) = -3\alpha\left(\frac{3\rho^\sigma}{4\pi}\right)^{\frac{1}{3}}} \quad \cdots\cdots (17)$$

The parameter α is considered to be an adjustable parameter to take account of the correlation term.

Density functional theory

Proof by Hohenberg and Kohn (Phys. Rev. 136, B864 (1964))

> **Theorem I**
>
> The total energy E of the non-degenerate ground state for a many electron system is uniquely determined by a functional of electron density $\rho(\mathbf{r})$

✡ Proof

First, it is assumed that two different external potential $V_{ext}(\mathbf{r})$ and $V'_{ext}(\mathbf{r})$ ($\neq V_{ext}(\mathbf{r}) + \text{const.}$) give the same ground state density ρ.

For V an V', we have

$$\hat{H}\Psi = (\hat{T} + V_{e\text{-}e} + V_{ext})\Psi = E\Psi \quad \cdots\cdots (1)$$

$$\hat{H}'\Psi = (\hat{T} + V_{e\text{-}e} + V_{ext})\Psi = E'\Psi' \quad \cdots\cdots (2)$$

The density is given by

$$N\int\cdots\int ds_1\, dx_2 \cdots dx_N\, \Psi^*(\mathbf{r}_1 s_1\, x_2 \cdots x_N)\Psi(\mathbf{r}_1 s\, x_2 \cdots x_N) = \rho(\mathbf{r}) \quad \cdots\cdots (1')$$

$$N\int\cdots\int ds_1\, dx_2 \cdots dx_N\, \Psi'^*(\mathbf{r}_1 s_1\, x_2 \cdots x_N)\Psi'(\mathbf{r}_1 s\, x_2 \cdots x_N) = \rho'(\mathbf{r}) \quad \cdots\cdots (2')$$

From the assumption we made, we have

$$\rho(\mathbf{r}) = \rho'(\mathbf{r}) \quad \cdots\cdots (3)$$

From the variational principle

$$E < \langle\Psi'|\hat{H}|\Psi'\rangle = \langle\Psi'|\hat{H}'|\Psi'\rangle + \langle\Psi'|(\hat{H} - \hat{H}')|\Psi'\rangle$$

Thus,
$$E < E' + \int dr^3\, \rho(\mathbf{r})\,(V_{ext}(\mathbf{r}) - V_{ext}(\mathbf{r}')) \quad \cdots\cdots (4)$$

Similarly, we have

$$E' < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | (\hat{H}' - \hat{H}) | \Psi \rangle$$

$$\longrightarrow \quad E' < E + \int d\mathbf{r}^3 \rho(\mathbf{r}) \left(V'_{ext}(\mathbf{r}) - V_{ext}(\mathbf{r}) \right) \quad \cdots\cdots (5)$$

By adding Eqs. (4) and (5), we see

$$E + E' < E + E' \quad \cdots\cdots (16)$$

This is a contradiction. The assumption $\rho = \rho'$ may not be correct. Therefore, it is concluded that for a given V the density ρ is uniquely determined as long as there is no degeneracy for the ground state.

<u>If ρ is v-representable</u>, which means that for a given ρ there is a potential V_{ext} giving the ρ, we have an one to one correspondence:

$$V_{ext} \rightleftarrows \rho \quad \cdots\cdots (17)$$

From Eqs. (1) and (1'), we can extend the correspondence as

$$V_{ext} \rightleftarrows \Psi \rightleftarrows \rho \quad \cdots\cdots (18)$$

Therefore

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | (\hat{T} + V_{e\text{-}e}) | \Psi \rangle + \int d\mathbf{r}^3 \rho(\mathbf{r}) V_{ext}(\mathbf{r})$$

$$= F_{HK}[\rho] + \int d\mathbf{r}^3 \rho(\mathbf{r}) V_{ext}(\mathbf{r}) \quad \cdots\cdots (19)$$

The theorem 2 has been proven under the v-representability condition.

> **Theorem 2**
>
> The total energy $E[\rho]$ of the ground state for a many electron system is obtained by minimizing the total energy functional of electron density ρ.

✱ Proof

For a trial wave function $\hat{\Psi}$, we have

$$\langle \hat{\Psi} | \hat{H} | \hat{\Psi} \rangle = \langle \hat{\Psi} | (\hat{T} + V_{e\text{-}e}) | \Psi \rangle + \int d\mathbf{r}^3 \hat{\rho}(\mathbf{r}) V_{ext}(\mathbf{r})$$

Eq.(19) $\longrightarrow$

ground state density

$$= F[\hat{\rho}] + \int d\mathbf{r}^3 \hat{\rho}(\mathbf{r}) V_{ext}(\mathbf{r}) \geq E[\rho_G]$$

Therefore, we obtain the following variational principle.

$$E[\rho_G] = \min_{\rho} E[\rho] \quad \cdots\cdots (20)$$

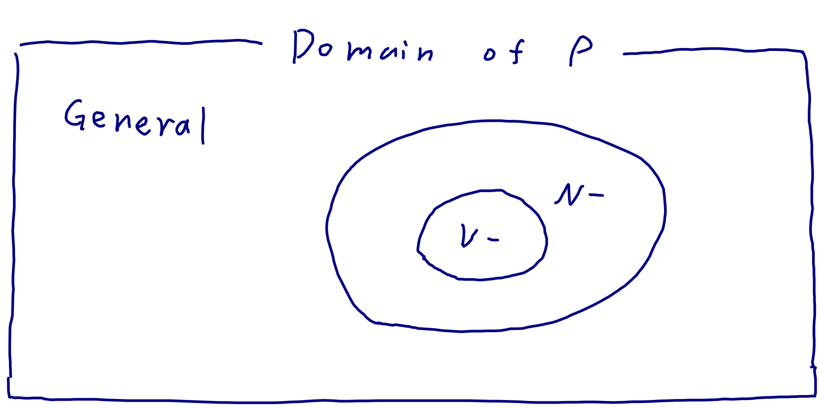
The theorem 2 has been proven.

✱ V- and N- representability

V-representability $\quad V \rightleftarrows \Psi \rightleftarrows \rho$

N-representability $\quad V \underset{?}{\overset{?}{\rightleftarrows}} \Psi \rightleftarrows \rho$

General case $\quad V \underset{?}{\overset{?}{\rightleftarrows}} \Psi \underset{?}{\overset{?}{\rightleftarrows}} \rho$



- In the proof of the HK theorem, we assumed the V-representability implicitly.
- Levy proved the theorem within the N-representability.

N-representability condition

For general cases, the mathematical condition is unknown for the v-representability.

For the N-representability, the conditions have been derived by Gilbert (PRB 12, 2111(1975)) as

Positivity	Charge conservation	Continuity
$\rho(\mathbf{r}) \geq 0$	$\int d\mathbf{r}^3 \rho(\mathbf{r}) = N$	$\int d\mathbf{r}^3 \left|\nabla \rho(\mathbf{r})^{\frac{1}{2}}\right|^2 < \infty$

$$\cdots\cdots \quad (21)$$

Construction of ρ by Harriman (Phy. Rev. A 24, 680 (1980))

Harriman showed that there are many orthonormal orbitals for the representation of an arbitrary density.

For simplicity, we consider an one-dimensional case.

An one-particle wave function ϕ_k is now given by

$$\phi_k(x) = [\sigma(x)]^{\frac{1}{2}} \exp[2\pi i k\, q(x)] \quad \cdots\cdots (22)$$

$$(x_1 \leq x \leq x_2)$$

$$\sigma(x) = \frac{1}{N}\rho(x) \quad \cdots\cdots (23)$$

$$q(x) = \int_{x_1}^{x} dx\, \sigma(x) \quad \cdots\cdots (24)$$

$k = 0, \pm 1, \pm 2, \pm 3, \cdots$

For all the ϕ_k, we have the same orbital density:

$$|\phi_k(x)|^2 = \sigma(x) \quad \cdots\cdots (25)$$

From Eq. (24), we see

$$q(x_1) = \int_{x_1}^{x_1} dx\, \sigma(x) = 0$$

$$q(x_2) = \int_{x_1}^{x_2} dx\, \sigma(x) = \int_{x_1}^{x_2} \frac{\rho(x)}{N} = 1$$

From the positivity of ρ, we have

$$0 = q(x_1) < q(x) < q(x_2) = 1 \quad \cdots\cdots (26)$$

Also, from Eq. (24), we have

$$\frac{dq(x)}{dx} = \sigma(x) \quad \cdots\cdots (27)$$

It is confirmed the orthonormality of ϕ_k as

$$\int_{x_1}^{x_2} dx\, \phi_k^*(x)\, \phi_{k'}(x) = \int_{x_1}^{x_2} dx\, \sigma(x) \exp[2\pi i\, q(x)(k'-k)]$$

$$= \int_{x_1}^{x_2} dx\, \exp[2\pi i\, q(x)(k'-k)] \frac{dq(x)}{dx}$$

$$= \int_0^1 dq\, \exp[2\pi i\, q(k'-k)]$$

$$k \neq k' \quad = \frac{1}{2\pi i(k'-k)} \Big[\exp(2\pi i\, q(k'-k))\Big]_0^1 = 0$$

$$k = k' \quad = 1 \longrightarrow \int_{x_1}^{x_2} dx\, \phi_k^*(x)\, \phi_{k'}(x) = \delta_{kk'} \quad \cdots\cdots (28)$$

By the Harriman method we see that Ψ can be changed while keeping a given ρ.

Using $\{\phi_k\}$, one can construct a many body wave function Ψ by a proper method such as CI and the electron density is given by

$$\rho(x) = \sum_k \lambda_k |\phi_k(x)|^2, \quad \sum_k \lambda_k = 1 \quad \cdots\cdots (29)$$

Constraint minimization by Levy

Proc. Natl. Acad. Sci (USA) 76, 6062 (1979).

☆ Theorem 1

Within N-representable ρ, the ground state energy E_{GS} is the lower bound of $E[\rho]$ definend by

$$E[\rho] = F[\rho] + \int dr^3\, V_{ext}(\mathbf{r})\, \rho(\mathbf{r}) \quad \cdots\cdots (30)$$

$$F[\rho] = \min_{\psi \to \rho} \langle \psi | (\hat{T} + V_{e\text{-}e}) | \psi \rangle \quad \cdots (31)$$

☆ Theorem 2

The ground state energy E_{GS} is represented by the ground state density ρ_{GS} as

$$E_{GS} = F[\rho_{GS}] + \int dr^3\, V_{ext}(\mathbf{r})\, \rho(\mathbf{r}) \quad \cdots (32)$$

The proof is given by a two-step minimization:

$$E_{GS} = \min_{\psi} \langle \psi | (\hat{T} + V_{e\text{-}e} + V_{ext}) | \psi \rangle \leftarrow$$ Variational principle for ψ

Even for the degenerate cas $\min_{\rho}$ is doable.

$$= \min_{\rho} \left\{ \min_{\psi \to \rho} \langle \psi | (\hat{T} + V_{e\text{-}e} + V_{ext}) | \psi \rangle \right\} \leftarrow$$ ρ is N-representative

ψ is changed while keeping ρ

$$= \min_{\rho} \left\{ \min_{\psi \to \rho} \langle \psi | (\hat{T} + V_{e\text{-}e}) | \psi \rangle + \int dr^3\, V_{ext}(\mathbf{r})\, \rho(\mathbf{r}) \right\}$$

$$= \min_{\rho} \left\{ F[\rho] + \int dr^3\, V_{ext}(\mathbf{r})\, \rho(\mathbf{r}) \right\}$$

The theorem 1 is proven by the first line = the fourth line. The ground state density ρ_{GS} is N-representative. Thus the fourth line proves the theorem 2.

Kohn – Sham method, Phys. Rev. 140, A1133 (1965)

The total energy and the electron density for a many electron system can be determined by solving self-consistently the Kohn – Sham equation with an effective single particle potential V_{eff} calculated by the electron density ρ. In the KS theory, the majority part of the kinetic energy is calculated by T_s which is the kinetic energy of a non-interacting system as follows:

$$E[\rho] = T[\rho] + J[\rho] + \int dr^3 \rho(\mathbf{r}) V_{ext}(\mathbf{r}) + E_{xc}^{(0)}[\rho]$$

$$= T_s + J[\rho] + \int dr^3 \rho(\mathbf{r}) V_{ext}(\mathbf{r}) + E_{xc}^{(0)} + (T - T_s)$$

$$= T_s + J[\rho] + \int dr^3 \rho(\mathbf{r}) V_{ext}(\mathbf{r}) + E_{xc}[\rho] \quad \cdots\cdots (33)$$

$$J = \frac{1}{2} \iint dr^3 dr'^3 \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad \cdots\cdots (34)$$

$$E_{xc}[\rho] = E_{xc}^{(0)}[\rho] + (T - T_s) \quad \cdots\cdots (35)$$

Comparing to Eq. (30), we have

$$F[\rho] = T_s + J[\rho] + E_{xc}[\rho] \quad \cdots (36)$$

Now we consider that T_s and ρ are calculated by <u>a single Slater determinant</u> which is the fictitious non-interacting system.

The one-particle orbital is called Kohn-Sham orbital.

$$\rho(\mathbf{r}) = 2\sum_i^{occ} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) \quad \cdots\cdots (37)$$

$$T_s = 2\sum_i^{occ} \langle \phi_i | \hat{T} | \phi_i \rangle \quad \cdots\cdots (38)$$

We now variationally optimize Eq. (33) with respect to the KS orbitals $\{\phi\}$ using Lagrange's multiplier method.

$$A = E[\rho] - \sum_{ij} \varepsilon_{ij} \left(\int dr^3 \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) - \delta_{ij} \right) \quad \cdots\cdots (39)$$

Noting that

$$\frac{\delta T_s}{\delta \phi_k^*} = 2 \hat{T} | \phi_k \rangle$$

$$\frac{\delta J}{\delta \phi_k^*} = \frac{\delta \rho}{\delta \phi_k^*} \frac{\delta}{\delta \rho} \left(\frac{1}{2} \iint dr dr'^3 \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) = 2 \phi_k(\mathbf{r}) \overbrace{\int dr'^3 \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}^{V_H(\mathbf{r})}$$

$$\frac{\delta}{\delta \phi_k^*} \left(\int dr^3 \rho(\mathbf{r}) V_{ext}(\mathbf{r}) \right) = \frac{\delta \rho}{\delta \phi_k^*} \frac{\delta}{\delta \rho} \left(\int dr^3 \rho(\mathbf{r}) V_{ext}(\mathbf{r}) \right) = 2 \phi_k(\mathbf{r}) \ V_{ext}(\mathbf{r})$$

$$\frac{\delta E_{xc}}{\delta \phi_k^*} = \frac{\delta \rho}{\delta \phi_k^*} \frac{\delta E_{xc}}{\delta \rho} = 2 \phi_k(\mathbf{r}) \frac{\delta E_{xc}}{\delta \rho}$$

we obtain $\dfrac{\delta A}{\delta \phi_k^*} = 0$ as

$$\Big(\hat{T} + \underbrace{V_H(\mathbf{r}) + V_{ext}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \rho}}_{V_{eff}(\mathbf{r})} \Big) \phi_k(\mathbf{r}) = \sum_j \varepsilon_{kj} \phi_j(\mathbf{r}) \quad \cdots\cdots (40)$$

Eq. (40) can be written by a matrix form:

$$F \rightarrow \begin{pmatrix} \hat{T} + V_{eff} & & & 0 \\ & \hat{T} + V_{eff} & & \\ & & \ddots & \\ 0 & & & \hat{T} + V_{eff} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_M \end{pmatrix} = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & & \\ \varepsilon_{21} & \varepsilon_{22} & & \\ & & \ddots & \\ & & & \varepsilon_{MM} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_M \end{pmatrix}$$

Noting that ε is Hermitian, and diagonalizing $\varepsilon = U \varepsilon_d U^\dagger$

$$F\phi = \varepsilon \phi \rightarrow F\phi = U \varepsilon_d U^\dagger \phi \rightarrow U^\dagger F U U^\dagger \phi = \varepsilon_d U^\dagger \phi$$

$\rightarrow F U^\dagger \phi = \varepsilon_d U^\dagger \phi$. By renaming $U^\dagger \phi \rightarrow \phi$, $\varepsilon_d \rightarrow \varepsilon$

One has a diagonal form $F\phi = \varepsilon \phi \quad \cdots\cdots (41)$

Thus, we obtain the KS equation

$$\boxed{\begin{aligned} &(\hat{T} + V_{eff})\,\phi_i(\mathbf{r}) = \varepsilon_i\,\phi_i(\mathbf{r}) && \cdots (42) \\ &V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d\mathbf{r}'^3 \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} && \cdots (43) \end{aligned}}$$

When the KS equation is solved self-consistently,

we can prove $\dfrac{\delta E}{\delta \rho} = 0$.

Proving the variational property is

the exercise 6.

Janak theorem Phys. Rev. B 18, 7165 (1978).

The single particle energy ε_i of the Kohn-Sham orbital is related to a partial derivative of the total energy with respect to an occupation number n_i.

$$\varepsilon_i = \frac{\partial E}{\partial n_i} \quad \cdots\cdots (44)$$

Proof: Let us assume that n_i can vary in between 0 and 1. Then, the density ρ is given by

$$\rho(\mathbf{r}) = \sum_k n_k\, \phi_k^*(\mathbf{r})\, \phi_k(\mathbf{r}) \quad \cdots\cdots (45)$$

where the index i includes both the spin and orbital indexes.

So the variation of E is given by

$$\delta E[\{n_k\},\{\phi_k\}] = \sum_k \int dr^3 \left[\left(\frac{\delta E}{\delta \phi_k}\right)_n \delta \phi_k \right] + \sum_k \left(\frac{\partial E}{\partial n_k}\right)_\phi \delta n_k \quad \cdots (46)$$

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where $(\ )_n$ and $(\ )_\phi$ stand for the partial derivatives with a set of fixed $\{n_k\}$ and $\{\phi_k\}$, respectively.

When the KS equation is solved, by the construction the first term becomes zero $\left(\frac{\delta E}{\delta \phi} = 0 \right)$.

Thus, we only have to consider the second term, and obtain the following formula:

$$\frac{\partial E}{\partial n_i} = \left(\frac{\partial E}{\partial n_i} \right)_\phi$$

$$= \int dr^3 \phi_i^*(\mathbb{r}) \hat{T} \phi_i(\mathbb{r}) + \int dr^3 \frac{\delta}{\delta \rho(\mathbb{r})} \left[\int dr'^3 V_{ext}(\mathbb{r}') \rho(\mathbb{r}') + J + E_{xc} \right]$$

$$= \int dr^3 \phi_i^*(\mathbb{r}) \hat{T} \phi_i(\mathbb{r}) + \int dr^3 \phi_i^*(\mathbb{r}) V_{eff}(\mathbb{r}) \phi_i(\mathbb{r})$$

$$= \varepsilon_i \qquad \cdots\cdots (47)$$

Thus, the Janak theorem states that in DFT the single particle energy ε_i corresponds to the energy per electron required the case that an infinitesimal quantity of electron is removed from the occupied state i, or the case that an infinitesimal quantity of electron is added to the unoccupied state i.