$$E = \int \left[ -\frac{\hbar^2}{2m} \nabla_1^2 \rho^r(r_1 r_2) \right]_{r=r_1} dr + \sum_\alpha \int \frac{q_\alpha(-e)\rho_1^r(r,r)\,dr}{4\pi\varepsilon_0 |R_\alpha - r|} + \frac{1}{2}\int \frac{\rho_1(r_1 r_1)\,\rho_1(r_2 r_2)\,dr_1 dr_2}{4\pi\varepsilon_0 |r_1 - r_2|}$$

$\Rightarrow$ r라 동일.

$$-\frac{1}{4}\int \frac{\rho_1^1(r_1 r_2)\,\rho_1^1(r_2 r_1)}{4\pi\varepsilon_0 |r_1 - r_2|} dr_1 dr_2 + \sum_{\alpha,\beta} \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 |R_\alpha - R_\beta|} + E_c(\rho^r).$$

$$\rho_1(r_1 r_2)?\quad \rho(r) \xrightarrow{\text{free } e^-} \phi_k(r) = \frac{1}{\sqrt{V}} e^{ikr} \xrightarrow{\rho_1(r_1 r_2)} \rho(r_1 r_2) = \frac{2}{V}\sum_{K}^{N/2} e^{i(k\cdot(r_1 - r_2))} \Rightarrow \rho\,(r_1 r_2).$$

$\left[\frac{2\pi}{L}n_x, \frac{2\pi}{L}n_y, \frac{2\pi}{L}n_z\right]$

$\rho(r) = \frac{r_1 + r_2}{2}$

$$\Rightarrow \frac{1}{2\pi^2}\int_0^{k_F \cdot S} \frac{K\cdot S \cdot 2\sin ks}{2}\, dks.$$

$\frac{4}{3}\pi k_F^3 = \rho(r).$

Tomas Fermi Dirac.

$$\int_0^{+1} e^{ik(r_1 - r_2)\cos\theta}\, d(\cos\theta)$$

$$= -\frac{e^{ik(r_1 - r_2)/3}}{ik(r_1 - r_2)}\Big|_{+1}^{-1}$$

$$= \frac{2\cdot \sin ks}{ks}$$

$$\frac{r_1 + r_2}{2} = \frac{2r_1}{2} = \frac{2r_2}{2} = r.$$

※ $\rho_1(r_1 r_2) = 3\rho(r)\left(\frac{\sin t - t\cos t}{t^3}\right)$, $r = \frac{r_1 + r_2}{2}$

↳ reduced first order density.

$t = k_F = S$

↳ $|r_1 - r_2|^{-1}$

K.E // Exchange form. $\Rightarrow$ 숙제.

$$\nabla_1^2 = \frac{1}{4}\nabla r + \nabla s^2 + \nabla r \nabla s.$$

$$\nabla_2^2 = \frac{1}{4}\nabla r + \nabla s^2 - \nabla r \nabla s.$$

$\rho(r) = \sum_i \phi_i^*(r)\phi(r)$, $e^{ik\cdot r}$

$$g(\rho(r)) = \frac{1}{1 + \frac{\nabla \rho(r)}{\rho(r)}}$$

$$\boxed{E = A\int \rho^{5/3}(r)\,dr + \sum_\alpha \int \frac{q_\alpha\, \rho(r)\,dr}{4\pi\varepsilon_0} + \frac{1}{2}\int \frac{\rho(r_1)\rho(r_2)}{4\pi\varepsilon_0 |r_1 - r_2|} dr_1 dr_2 - \beta\int \rho^{4/3}(r)\,dr}$$

exchange

$$+ \sum_{\alpha,\beta} \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 |R_\alpha - R_\beta|} + E_c(\rho).$$

reference state

Local density Approximation (LDA) : free $e^-$의 K.E contribution 적다

generalized gradient Approximation (GGA)

Hybrid

$$E = \underbrace{\sum^N \langle \phi_i | -\frac{\hbar^2}{2m}\nabla^2 | \phi_i \rangle}_{} + \sum_\alpha \int \frac{q_\alpha(-e)\rho(r)}{4\pi\varepsilon_0 |R_\alpha - r|} dr + \frac{1}{2}\int \frac{\rho(r_1)\rho(r_2)}{4\pi\varepsilon_0 |r_1 - r_2|} dr_1 dr_2$$

$\rho(r) = \sum^N \phi^*(r)\phi(r)$

$$-\frac{1}{2}\sum \int \frac{\phi_i^*(r_1)\phi_j(r_1)\,\phi_i(r_2)\phi_j(r_2)}{4\pi\varepsilon_0 |r_1 - r_2|} dr_1 dr_2 + \sum_\alpha \sum_\beta \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 |r_1 - r_2|} + E_c(\phi\phi^*)$$

↳ $\rho(r)$

$$\frac{\partial E}{\partial \phi_i^*} = \frac{\partial E}{\partial \rho}\frac{\partial \rho}{\partial \phi^*} = \sum \phi_i^*(r)\phi(r).$$

$$= \phi_i(r).$$