Short preview of the Density functional theory and Kohn-Sham equation

$$E = \sum_{\lambda=1}^{N} \int \psi_\lambda^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) \right) \psi_\lambda(\mathbf{r}) d^3\vec{r} + \frac{1}{2} \sum_{\lambda=1}^{N} \sum_{\mu=1}^{N} \iint \frac{\psi_\lambda^*(\mathbf{r}_1)\psi_\mu^*(\mathbf{r}_2)\psi_\lambda(\mathbf{r}_1)\psi_\mu(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2 + E_{xc}[\rho]$$

$$E_{xc}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}[\rho(\mathbf{r})] d^3\vec{r}$$

Exchange-correlation energy density

Exchange-correlation energy functional

Exercise and Discussion (장형윤)

- Suppose we have energy functional which consists of N orthonormal orbital, $\int \psi_\lambda^*(\vec{r})\psi_\mu(\vec{r})d^3\vec{r} = \delta_{\mu\lambda}$.

$$E = \sum_{\lambda=1}^{N}\int \psi_\lambda^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi_\lambda(\mathbf{r})d^3\vec{r} + \frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\iint \frac{\psi_\lambda^*(\mathbf{r}_1)\psi_\mu^*(\mathbf{r}_2)\psi_\lambda(\mathbf{r}_1)\psi_\mu(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\vec{r}_1 d^3\vec{r}_2 + E_{xc}[\rho],$$

$$\text{where } E_{xc}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}[\rho(\mathbf{r})]d^3\vec{r} \quad \text{and} \quad \rho(\mathbf{r}) = \sum_{\lambda=1}^{N}\psi_\lambda^*(\mathbf{r})\psi_\lambda(\mathbf{r})\ .$$

- Using the Euler-Lagrange equation for the calculus of variations, derive the self-consist field (SCF) equation for the N orbitals.

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) + \left(\sum_{\mu=1}^{N}\int \frac{\psi_\mu^*(\mathbf{r}_2)\psi_\mu(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d^3\vec{r}_2\right)\psi_\lambda(\mathbf{r}) + V_{xc}[\rho(\mathbf{r})]\psi_\lambda(\mathbf{r}) = \varepsilon_\lambda\psi_\lambda(\mathbf{r})\ , \text{ where}$$

$$V_{xc}[\rho(\mathbf{r})] = \left(\varepsilon_{xc}[\rho(\mathbf{r})] + \rho\frac{d\varepsilon_{xc}}{d\rho}\right)$$

Exchange energy of the uniform electron gas

- Bloch & Dirac (1920~1930), for uniform spin-unpolarized electron liquid

$$E_x^{\,0} = \int \rho(\vec{r})\varepsilon_x[\rho]d^3\vec{r}$$

$$\varepsilon_x[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} e^2\left(\rho(\vec{r})\right)^{1/3} = \left[-\frac{0.91664}{(3/4\pi)^{1/3}} n^{1/3}(\vec{r})a_0\right]\left(\frac{e^2}{2a_0}\right) = \left[-1.4774 n^{1/3}(\vec{r})a_0\right]\left(\frac{e^2}{2a_0}\right)$$

LDA

- The exchange energy density

$$\varepsilon_{xc}[\rho(\vec{r})] = \left[-\frac{0.91664}{(3/4\pi)^{1/3}}\rho^{1/3}(\vec{r})a_0 + 0.0622\ln\left(\frac{3}{4\pi}\frac{1}{\rho^{1/3}(\vec{r})a_0}\right) - 0.096 + O\left(\frac{1}{\rho(\vec{r})}\right)\right]\left(\frac{e^2}{2a_0}\right)$$

The equation is

- It is the differential equation eigenvalue problem. Once the boundary condition is specified (for example, fixed value or periodic boundary condition), we can determine the eigenfunctions (ψ_μ, $\mu = 1,2,\ldots,N$) and eigenvalues (ε_μ, $\mu = 1,2,\ldots,N$) .

- It is non-linear differential equation. We cannot make it inversion of the operator. We solve it through the self-consistent field procedure (SCF procedure).

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) + V_H[\rho(\mathbf{r})]\psi_\lambda(\mathbf{r}) + V_{xc}[\rho(\mathbf{r})]\psi_\lambda(\mathbf{r}) = \varepsilon_\lambda\psi_\lambda(\mathbf{r}) \text{ , where}$$

$$V_H[\rho(\mathbf{r})] = \sum_{\mu=1}^{N}\int \frac{\psi_\mu^*(\mathbf{r}')\psi_\mu(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\vec{r}_2 \quad , \quad V_{xc}[\rho(\mathbf{r})] = \left(\varepsilon_{xc}[\rho(\mathbf{r})] + \rho\frac{d\varepsilon_{xc}}{d\rho}\right)$$

The equation is

- Mathematically, the Euler-Lagrange equation requires the SCF procedure for N orbitals.
- However, the number of eigenvalues and eigenfunctions are infinite. Visit the mathematical textbook for the differential equation part.

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) + V_H[\rho(\mathbf{r})]\psi_\lambda(\mathbf{r}) + V_{xc}[\rho(\mathbf{r})]\psi_\lambda(\mathbf{r}) = \varepsilon_\lambda\psi_\lambda(\mathbf{r}),$$

where $\lambda = 1, 2, ..., N, N+1, N+1, ...\infty$

Occupied orbitals versus unoccupied ones.

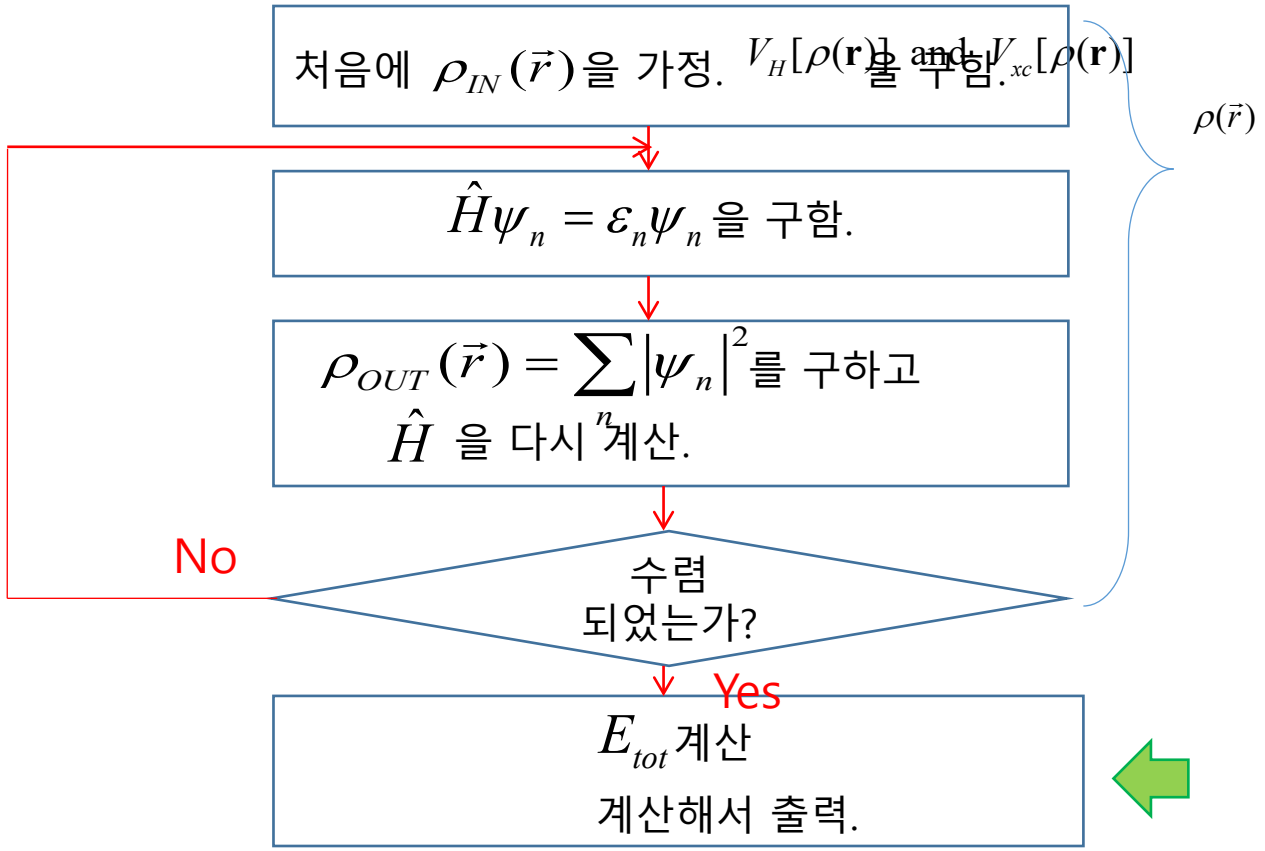
- Among the infinite number of eigenfunctions, let us select the N orbitals with lowest eigenvalues.

$$\varepsilon_1 \ , \quad \psi_1(\vec{r})$$
$$\varepsilon_1 \ , \quad \psi_1(\vec{r})$$
$$\varepsilon_1 \ , \quad \psi_1(\vec{r})$$
$$\vdots$$
$$\varepsilon_N \ , \quad \psi_N(\vec{r})$$
$$\varepsilon_{N+1} \ , \quad \psi_{N+1}(\vec{r})$$
$$\varepsilon_{N+2} \ , \quad \psi_{N+2}(\vec{r})$$
$$\vdots$$

$$\rho(\vec{r}) = \sum_{\lambda=1}^{N} |\psi_\infty(\vec{r})|^2 = \sum_{\lambda=1}^{\infty} f_\lambda \, |\psi_\infty(\vec{r})|^2$$

$$f_\lambda = \begin{cases} 1 & \text{for } \lambda \le N \\ 0 & \text{for } \lambda > N \end{cases}$$

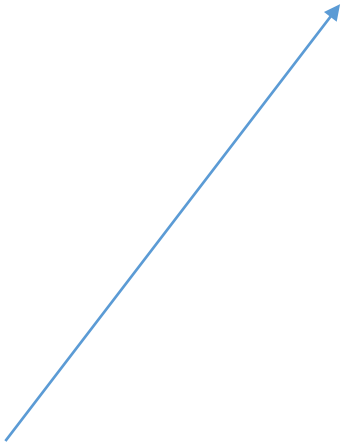
SCF procedure



Physical implication

- It is intended to remove the self-interaction

$$E=\sum_n\int\psi_n^*(\vec{r})\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi_n(\vec{r})d^3\vec{r}+\int U_{atom}(\vec{r})(-e)\rho(\vec{r})d^3\vec{r}+\frac{1}{2}\int\int\frac{e^2\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3\vec{r}d^3\vec{r}'+\int\varepsilon_{excorr}(\vec{r})\rho(\vec{r})d^3\vec{r}+\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{Z_iZ_je^2}{|\vec{R}_i-\vec{R}_j|}$$

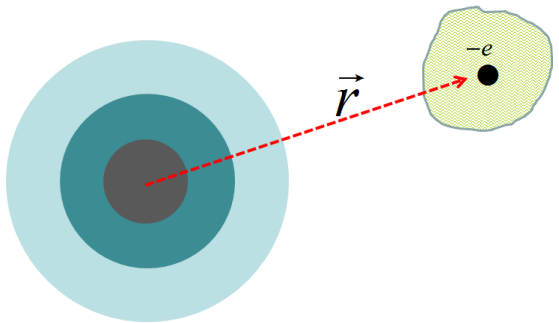


$$\left(-\frac{1}{2}\nabla^2+V(\mathbf{r})+V_H(\mathbf{r})\right)\psi_\lambda(\mathbf{r})-\int\Omega(\mathbf{r},\mathbf{r}')\psi_\lambda(\mathbf{r}')d^3\vec{r}'=\varepsilon_\lambda\psi_\lambda(\mathbf{r})$$

The long-range behaviour of v_{xc}

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3\vec{r}' + v_{xc}[\rho(\vec{r})]\right]\psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r})$$

$$-\frac{Ne^2}{r} \qquad +\frac{Ne^2}{r} \qquad -\frac{e^2}{r}$$



$$+\frac{(N-1)e^2}{r}$$

Exchange-Correlation energy density functional

- From the Euler-Langrange equation

$$\frac{\delta \tilde{E}}{\delta \psi_\lambda^*} = 0$$

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) + \left(\sum_{\mu=1}^{N}\int \frac{\psi_\mu^*(\mathbf{r}_2)\psi_\mu(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|} d^3\vec{r}_2\right)\psi_\lambda(\mathbf{r}) + \left(\varepsilon_{xc}[\rho(\mathbf{r})] + \rho\frac{d\varepsilon_{xc}}{d\rho}\right)\psi_\lambda(\mathbf{r}) = \varepsilon_\lambda\psi_\lambda(\mathbf{r})$$

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) + V_H[\rho(\mathbf{r})]\psi_\lambda(\mathbf{r}) + V_{xc}[\rho(\mathbf{r})]\psi_\lambda(\mathbf{r}) = \varepsilon_\lambda\psi_\lambda(\mathbf{r})$$

- Show that

$$E = \sum_{\lambda=1}^{N}\varepsilon_\lambda + \int \rho(\mathbf{r})\varepsilon_{xc}[\rho(\mathbf{r})]d^3\vec{r} - \int \rho(\mathbf{r})V_{xc}[\rho(\mathbf{r})]d^3\vec{r}$$

Many many developments over decades

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}[\rho(\mathbf{r})]d^3\vec{r}$$

Many theorists have devoted to find this functional form.

How ?

The theory, QFT treatment of interacting many bodies.

Exchange-correlation density functional

I. Exchange and correlation

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] = \int d^3\vec{r}\,\rho(\vec{r})\varepsilon_x[\rho] + \int d^3\vec{r}\,\rho(\vec{r})\varepsilon_c[\rho]$$

II. The action of the exchange potential, a non-local interaction

To remove the self interaction

$$E=\sum_n\int\psi_n^*(\vec{r})\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi_n(\vec{r})d^3\vec{r}+\int U_{atom}(\vec{r})(-e)\rho(\vec{r})d^3\vec{r}+\frac{1}{2}\int\int\frac{e^2\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3\vec{r}d^3\vec{r}'+\int\varepsilon_{excorr}(\vec{r})\rho(\vec{r})d^3\vec{r}+\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{Z_iZ_je^2}{|\vec{R}_i-\vec{R}_j|}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2+U_{atom}(\vec{r})+\int\frac{e^2\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3\vec{r}'+v_{xc}(\vec{r})\right)\psi_n(\vec{r})=\varepsilon_n\psi_n(\vec{r})\ ,$$

$$v_{xc}(\vec{r})=\varepsilon_{excorr}(\vec{r})+\rho\frac{d\varepsilon_{excorr}}{d\rho}$$

$$\approx\rho^{1/3}(\vec{r})$$

Notes for exchange-correlation energy

I. The exchange-correlation energy and its density

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] = \int d^3\vec{r}\,\rho(\vec{r})\varepsilon_x[\rho] + \int d^3\vec{r}\,\rho(\vec{r})\varepsilon_c[\rho]$$

Two-body energy of the uniform electron gas (Lecture Note(2019))

- The exchange energy

$$E_{xc} = -\frac{9n}{4} N \int d^3\vec{x} \frac{1}{k_F^3} k_F \frac{e^2}{x} \left[\frac{\sin x - x\cos x}{x^3} \right]^2 = -\frac{3Ne^2}{\pi} k_F \int_0^\infty \frac{(\sin x - x\cos x)^2}{x^5} dx = -N \frac{3e^2}{4\pi} k_F$$

- Average exchange energy

$$E_{xc}/N = -\frac{1}{r_s} 2 \frac{3}{4\pi} \left(\frac{9\pi}{4} \right)^{1/3} \left(\frac{e^2}{2a_0} \right) = -\frac{0.916}{r_s} \left(\frac{e^2}{2a_0} \right) = -\frac{0.916}{(a_0/d)} \left(\frac{e^2}{2a_0} \right)$$

- What is the name of this energy quantum $e^2/2a_0$?
- [Ref, Aschroft &Mermin, Ch 17]

Some discussions on high density limit

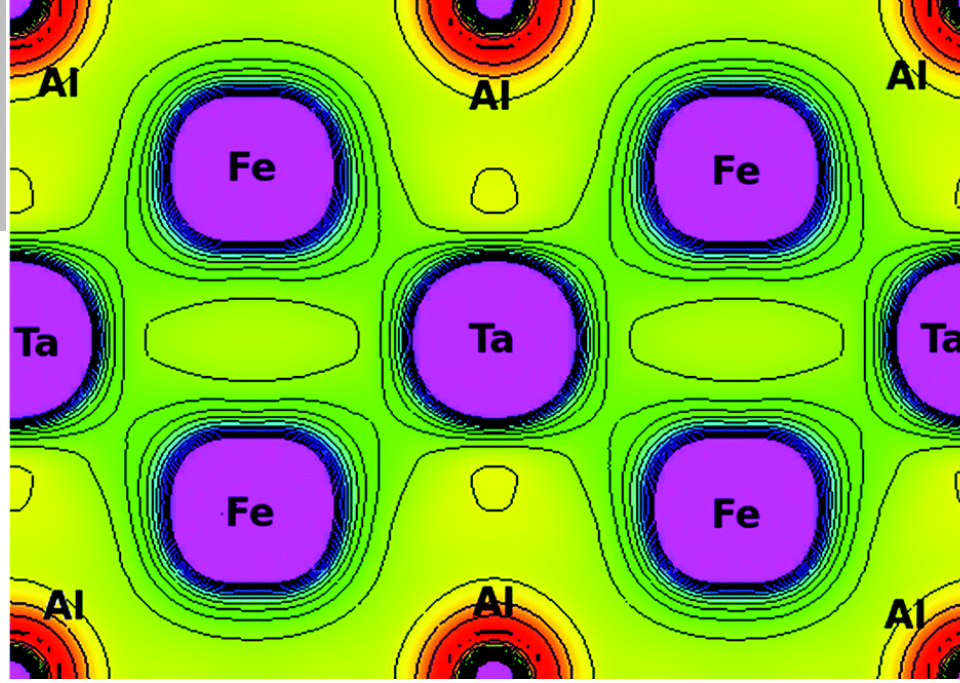
- The average energy per particle of the interacting electron liquid with the constant density or uniform positive background. In this circumstances, the Hatree energy is just a constant, and then

$$E/N = \left[\frac{2.21}{r_s^2} - \frac{0.91664}{r_s} + 0.0622 \ln(r_s) - 0.096 + O(r) \right] \left(\frac{e^2}{2a_0} \right)$$

- The dimensionless parameters

$$\frac{4\pi}{3} r_s^3 = \frac{N}{V} \Rightarrow r_s = \left(\frac{3}{4\pi} n \right)^{1/3} \frac{1}{a_0}$$

In a realistic solid



- The density $n(\vec{r})$ is not costant, and then

$$E=\left[\sum_s\int d^3\vec{r}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\vec{r}^{\,2}}\right)\rho_{ss'}(\vec{r},\vec{r}')\right]_{\vec{r}'=\vec{r},s=s'}$$

$$+\int n(\vec{r})U(\vec{r})d^3\vec{r}+\frac{1}{2}e^2\iint d^3\vec{r}d^3\vec{r}'\frac{\rho(\vec{r})\rho(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}$$

$$+\int n(\vec{r})\varepsilon_{xc}[n(\vec{r})]d^3\vec{r}$$

- The exchange energy density

$$\varepsilon_{xc}[n(\vec{r})]=\left[-\frac{0.91664}{(3/4\pi)^{1/3}}n^{1/3}(\vec{r})a_0+0.0622\ln\left(\frac{3}{4\pi}\frac{1}{n^{1/3}(\vec{r})a_0}\right)-0.096+O\left(\frac{1}{n(\vec{r})}\right)\right]\left(\frac{e^2}{2a_0}\right)$$

Notes for exchange-correlation energy

I. Local density approximation (LDA)

$$E_{xc}^{LDA}[\rho] = E_x^{LDA}[\rho] + E_c^{LDA}[\rho] = \int \varepsilon_x^{LDA}(\rho) d^3\vec{r} + \int \varepsilon_c^{LDA}(\rho) d^3\vec{r}$$

$$E_x^{LDA}[\rho] = \int \varepsilon_x^{LDA}(\rho) d^3\vec{r}$$

$$= \int -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3} \rho^{4/3}(\vec{r}) d^3\vec{r}$$

$$E_c^{LDA}[\rho] = \int \varepsilon_c^{LDA}(\rho) d^3\vec{r}$$

$$= \int -A\rho(\vec{r})(1+\alpha_1 r_s)$$

$$\times \ln\left[1 + \frac{1}{A\left(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^{2}\right)}\right] d^3\vec{r}$$

,where $r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$ and $A, \alpha_1, \beta_1, \beta_2, \beta_3, \beta_4$ are fixed parameters.

Notes for exchange-correlation energy

I. Generalized Gradient Approximation (GGA)

$$E_x^{GGA}[\rho]=\int \rho(\vec{r})\,\varepsilon_x^{LDA}(\rho)\,F_x^{GGA}(\rho,s)\,d^3\vec{r},\ \text{where } s(\vec{r})=\frac{|\nabla\rho(\vec{r})|}{\rho(\vec{r})^{4/3}}$$

II. Becke 88 Exchange

$$E_x^{B88}[\rho]=\int \rho(\vec{r})\,\varepsilon_x^{LDA}(\rho)\,F_x^{B88}(\rho,s)\,d^3\vec{r}$$

$$F_x^{B88}(\rho,s)=1+\frac{2}{3}\left(\frac{4\pi}{3}\right)^{1/3}\beta\frac{s^2}{1+6\beta s\sinh^{-1}(s)}$$

,where $\beta=0.0042E_H$

$$\varepsilon_x^{LDA}(\rho)=-\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\rho^{4/3}(\vec{r})$$

$$E_x^{B88}[\rho]=-\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{7/3}(\vec{r})$$

PBE Exchange Functional

$$E_x^{PBE}[\rho] = \int \rho(\vec{r})\,\varepsilon_x^{LDA}(\rho)\,F_x^{PBE}(\rho,s)\,d^3\vec{r}$$

$$F_x^{PBE}(\rho,s) = 1+\kappa-\frac{\kappa}{1+\frac{\mu s^2}{\kappa\left(48\pi^2\right)^{2/3}}}$$

,where $\mu = 0.21951$ and $\kappa = 0.804$

$$\varepsilon_x^{LDA}(\rho) = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\rho^{4/3}(\vec{r})$$

$$E_x^{PBE}[\rho] = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{7/3}(\vec{r})\left[1+\kappa-\frac{\kappa}{1+\frac{\mu s^2}{\kappa\left(48\pi^2\right)^{2/3}}}\right]d^3\vec{r}$$

PBE Correlation Functional

$$E_c^{PBE}\left[\rho_\uparrow,\rho_\downarrow\right] = \int \rho(\vec{r})\left[\varepsilon_c^{LDA}(\rho)+H^{PBE}(r_s,\zeta,t)\right]d^3\vec{r}$$

,where

$$\zeta = \frac{\rho_\uparrow,\rho_\downarrow}{\rho}$$

$$t = \frac{|\nabla\rho|}{2k_s\phi}$$

$$k_s = \sqrt{\frac{4k_F}{\pi}}$$

$$k_F = \sqrt[3]{3\pi^2\rho}$$

$$\phi = \frac{(1+\zeta)^{2/3}+(1-\zeta)^{2/3}}{2}$$

$$H^{PBE} = \gamma\phi^3\ln\left[1+\frac{\beta}{\gamma}t^2\frac{1+At^2}{1+At^2+A^2t^4}\right]$$

$$A = \frac{\beta}{\gamma\left(e^{-\varepsilon_c^{LDA}/\gamma\phi^3}-1\right)}$$

$\gamma = 0.031091$ and $\beta = 0.066725$

PW91 Exchange Functional

$$E_x^{PW91}[\rho] = \int \rho(\vec{r})\,\varepsilon_x^{LDA}(\rho)\,F_x^{PW91}(\rho,s)\,d^3\vec{r}$$

$$F_x^{PW91}(\rho,s) = \frac{bs^2 - (b-\beta)s^2 e^{-cs^2} - 10^{-6}s^4}{1 + 6b\sinh^{-1}(s) - 10^{-6}\dfrac{s^4}{A_s}}$$

,where

$b = 0.0042$

$\beta = 5(36\pi)^{-5/3}$

$c = 1.6455$

$$A_s = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}$$

$$\varepsilon_x^{LDA}(\rho) = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\rho^{4/3}(\vec{r})$$

$$E_x^{PW91}[\rho] = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{7/3}(\vec{r})\frac{bs^2 - (b-\beta)s^2 e^{-cs^2} - 10^{-6}s^4}{1 + 6b\sinh^{-1}(s) - 10^{-6}\dfrac{s^4}{A_s}}\,d^3\vec{r}$$

Exchange in the spin polarized system

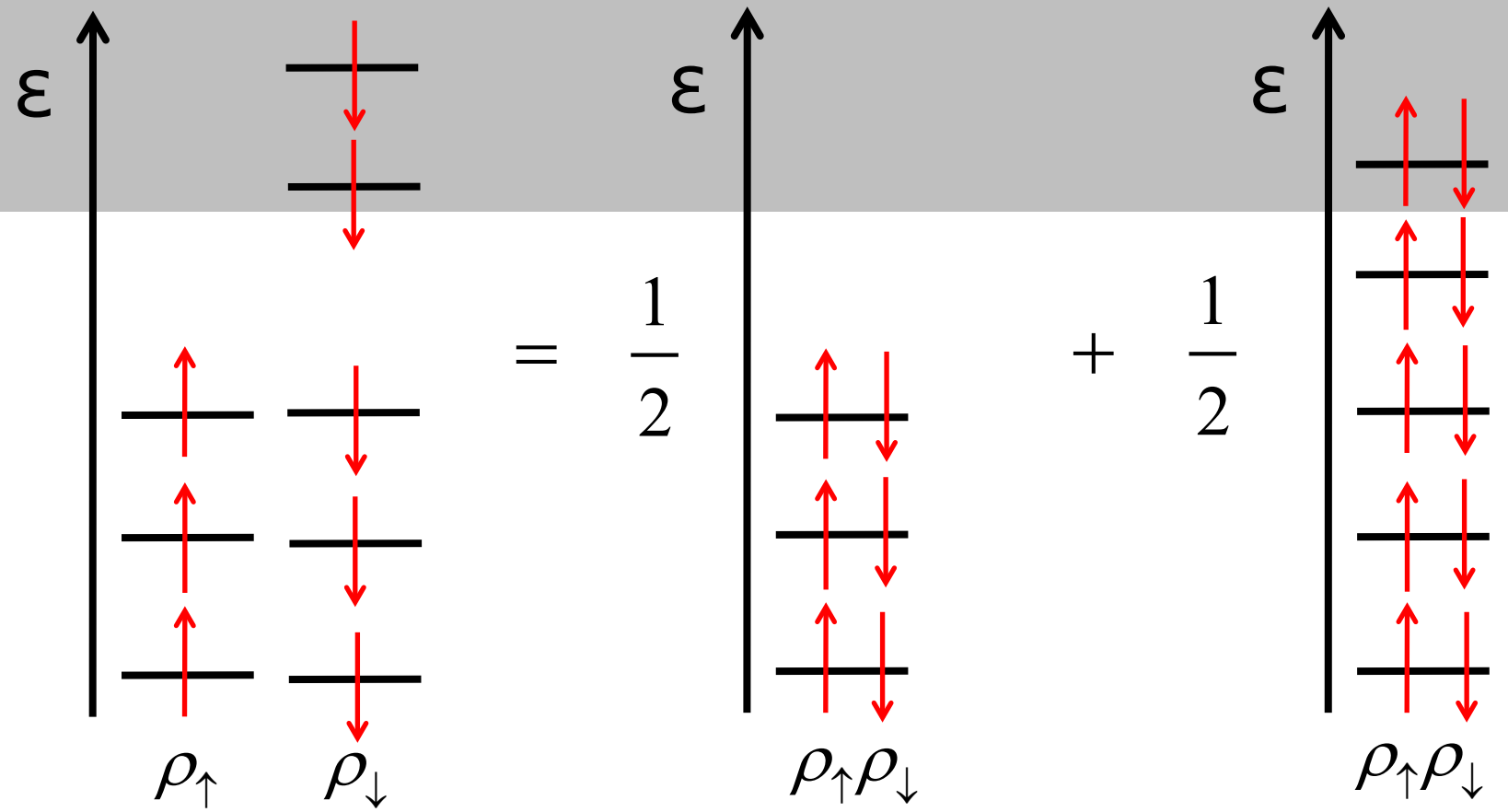
Filatov & Thiel, *Molecular Physics*, 91, 847(1997)

Dirac, *Comb. Phil. Soc. Math. Phys. Sci*, 26, 376(1930)

$$E_x^{Dirac}[\rho_\uparrow, \rho_\downarrow] = \frac{1}{2}E_x^{0}[2\rho_\uparrow] + \frac{1}{2}E_x^{0}[2\rho_\downarrow] = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3} e^2 \int [\rho_\uparrow^{4/3} + \rho_\downarrow^{4/3}] d^3\vec{r}$$

$$E_x[\rho_\uparrow, \rho_\downarrow] = (Exchange\ between\ spin-up\ orbitals) + (Exchange\ between\ spin-down)$$

$$E[\rho_\uparrow, \rho_\downarrow] = \frac{1}{2}\underbrace{E_x{}^0[2\rho_\uparrow]}_{\substack{up-spin\ 전자숫자\\ 만큼으로\ 구성된\\ Spin\text{-}compensated\\ case}} + \frac{1}{2}\underbrace{E_x{}^0[2\rho_\downarrow]}_{\substack{down-spin\ 전자숫자\\ 만큼으로\ 구성된\\ Spin\text{-}compensated\\ case}}$$



$$E[\rho_\uparrow,\rho_\downarrow]=\frac{1}{2}\underbrace{E_x{}^0[2\rho_\uparrow]}_{\substack{up-spin\ 전자숫자\ 만큼으로\ 구성된\ Spin-compensated\ case}}+\frac{1}{2}\underbrace{E_x{}^0[2\rho_\downarrow]}_{\substack{down-spin\ 전자숫자\ 만큼으로\ 구성된\ Spin-compensated\ case}}$$