Lecture FYS4480, October 27, 2023

Electron-gas in 3dim

$$\langle H \rangle = \langle T \rangle + \langle H_I \rangle$$

$$\langle T \rangle = \frac{V \hbar^2 k_F^5}{\pi^2 10 m}$$

$$a_0 = \frac{\hbar^2}{2me^2} \qquad 1Ry = \frac{me^4}{2\hbar^2}$$

$$= 13.6 \, eV$$

$$\rho = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

$$= \frac{3}{4\pi r_s^3}$$

$$\langle T \rangle = N \cdot 2.21 \left(\frac{a_0}{r_s} \right)^2 \cdot 1 \, Ry$$

$$\langle H_I \rangle = \ldots$$

$$8\pi \int_0^{k_F} d^3p \int_0^p dk \sum_l \left(\frac{k}{p}\right)^{2l+2} \frac{1}{2l+1}$$

$$= 8\pi^2 k_F^4 \sum_l \frac{1}{(2l+1)(2l+3)}$$

$$\sum_l \frac{1}{(2l+1)(2l+3)} = \frac{1}{2} \sum_l \left(\frac{1}{2l+1} - \frac{1}{2l+3} \right)$$

$$= \frac{1}{2} + \frac{1}{2} \sum_{l=0}^{\infty} \left(\frac{1}{2l+3} - \frac{1}{2l+3} \right)$$

$$= 1/2$$

$$\Rightarrow \langle H_I \rangle = -\frac{e^2 V k_F^4}{4\pi^3}$$

using a_0 and r_s

$$\langle H_1 \rangle = -0.916 \cdot a_0/r_s \cdot N \cdot \mathrm{Ry}$$

$$\frac{\langle H \rangle}{N} = \left[\frac{2.21}{(r_s/a_0)^2} - \frac{0.916}{(r_s/a_0)} \right] \mathrm{Ry}$$

$$\frac{\langle H_1 \rangle}{N} = -e^2 \rho^{-1} \frac{k_F^4}{4\pi^3} \Leftarrow \propto \rho^{4/3}$$

$$\boxed{\rho = N/V} \quad = -\text{const}\, \rho^{1/3}$$

→ local density approx for the exchange energy

$$P = -\left(\frac{\partial E_0^{HF}}{\partial V}\right)_N$$

$$E_0^{HF} = \langle T \rangle - \text{const}\, \rho^{4/3}$$

$$B = -V\left(\frac{\partial P}{\partial V}\right)_N$$

Density functional theory,

$$\Big[t(\vec{r}) + v_{ext}(\vec{r}) + \int d\vec{r}\,'\rho(\vec{r}\,') \times v(\vec{r},\vec{r}\,') + V_{xc}[\rho](\vec{r}) \Big] \psi_k(\vec{r})$$

KS = Kohn-Sham

$$= \varepsilon_k \psi_k^{KS}(\vec{r})$$

Hartree-Fock theory

$$\left[t(\vec{r}) + v_{ext}(\vec{r}) + u^{HARTREE}(\vec{r}) \right]$$

$$\times \psi_k(\vec{r}) + \int d\vec{r}\,' u^{FOCK}(\vec{r}) \Phi_k^{HF}(\vec{r}\,')$$

$$= \varepsilon_k^{HF} \psi_k^{HF}(\vec{r})$$

$$u^{HARTREE}(\vec{r}) =$$

$$\sum_{i \leq F} \int d\vec{r}\,' |\psi_i(\vec{r}\,')|^2 v(\vec{r}, \vec{r}\,')$$

$$\rho(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2 \Bigg| = \int d\vec{r}\,' \rho(\vec{r}\,') v(\vec{r}, \vec{r}\,')$$

$$u^{FOCK}(\vec{r}) = -\sum_{k \le F} \psi_k^*(\vec{r}\,')\, v(\vec{r},\vec{r}\,') \times \psi_k(\vec{r})$$

Exchange term.

cannot write it as some thing proportional to $\rho(\vec{r})$

$$\left[\langle \Phi_0 | \rho(\vec{r}) | \Phi_0 \rangle = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2 \right.$$

Total energy with an SD

$$\Phi_0 = \prod_{i=1}^{N} a_i^{+} |0\rangle$$

$$\Phi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \cdots & \psi_1(\vec{r}_N) \\ \psi_2(\vec{r}_1) & \vdots & - & - \\ \vdots & \vdots & - & - \\ \psi_N(\vec{r}_1) & \vdots & & \psi_N(\vec{r}_N) \end{vmatrix}$$

$$\langle \Phi_0 | H | \Phi_0 \rangle = E_0^{HF} \qquad H|\Phi_0\rangle \neq E_0|\Phi_0\rangle$$

$$= \sum_{i \leq F} \langle i | h_0 | i \rangle + \frac{1}{2} \sum_{ij} \left\{ \langle ij | v | ij \rangle - \langle ij | v | ji \rangle \right\}$$

$$\frac{1}{2}\sum_{i'j'} \langle i'j' | v | i'j' \rangle =$$

$$\frac{1}{2}\sum_{i'j'} \int d\vec{r} \int d\vec{r}\,' \, \psi_{i'}^*(\vec{r})\, \psi_{j'}^*(\vec{r}\,')\, v(\vec{r},\vec{r}\,')$$

$$\times \psi_{i'}(\vec{r})\, \psi_{j'}(\vec{r}\,')$$

$$= \frac{1}{2} \int d\vec{r} \int d\vec{r}\,' \, \rho(\vec{r})\, \rho(\vec{r}\,')\, v(\vec{r},\vec{r}\,')$$

$$\frac{1}{2}\sum_{i'j'} \langle i'j' | v | j'i' \rangle =$$

$$\frac{1}{2}\sum_{i'j'} \int d\vec{r} \int d\vec{r}\,' \, \psi_{i'}^*(\vec{r})\, \psi_{j'}^*(\vec{r}\,')\, v(\vec{r},\vec{r}\,')$$

$$\times \psi_{i'}(\vec{r}\,')\, \psi_{j'}(\vec{r})$$

HF-energy:

$$E_0^{HF} = \sum_{i \leq F} \varepsilon_i^{HF} - \frac{1}{2} \sum_{ij} \langle ij | v | ij \rangle$$

$$\boxed{+ \frac{1}{2} \sum_{ij} \langle ij | v | ji \rangle}$$

$$= \sum_{i \leq F} \varepsilon_i^{HF} - \frac{1}{2} \int d\vec{r} \int d\vec{r}\,' \rho(\vec{r}) \rho(\vec{r}\,') \times v(\vec{r}, \vec{r}\,') + \boxed{E_{xc}^{HF}}$$

$$E_0^{KS} = \sum_{i \leq F} \varepsilon_i^{KS} - \frac{1}{2} \int d\vec{r}\, d\vec{r}\,' \rho(\vec{r}) \rho(\vec{r}\,') \times v(\vec{r}, \vec{r}\,')$$

$$+ E_{xc}[\rho] - \int d\vec{r}\, V_{xc}[\rho](\vec{r})$$

E_{xc} = the exchange correlation energy which replaces $\frac{1}{2}\sum_{ij} \langle ij | v | ji \rangle$

(the exchange term in HF theory)

$$V_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

instead of

$$E[\Phi_0] = \arg\min_{\Phi_0} \langle \Phi_0 | H | \Phi_0 \rangle$$

(HF)

$$E[\rho] = \arg\min_{\rho} \langle \Phi_0 | H | \Phi_0 \rangle$$

defined by ρ

in the non-interacting case

$$H = T + V_{ext}$$

$$T = \sum_i -\frac{\nabla_i^2}{2} \qquad V_{ext} = \sum_i v_{ext}(\vec{r}_i)$$

$$E[\rho] = T[\rho] + \int d\vec{r}\, v_{ext}(\vec{r})\, \rho(\vec{r})$$

variation wrt ρ

$$\frac{\delta T}{\delta \rho} + v_{ext}(\vec{r}) = \lambda \rho$$

Lagrange multiplier

$$h_0\, \psi_i(\vec{r}) = \varepsilon_i\, \psi_i(\vec{r})$$

$$H_0 |\underline{\Phi_0}\rangle = E_0 |\Phi_0\rangle$$

$$\langle \Phi_0 | T | \Phi_0 \rangle \neq \langle \Psi_0 | T | \Psi_0 \rangle$$

$H|\Phi_0\rangle \neq E|\Phi_0\rangle$ $\qquad$ $H|\Psi_0\rangle = E|\Psi_0\rangle$

$$H = T + V_{ext} + H_I$$

$$E[\rho] = T[\rho] + \int d\vec{r}\,\rho(\vec{r})\,v_{ext}(\vec{r})$$

$$+ \frac{1}{2}\int d\vec{r}\int d\vec{r}\,'\rho(\vec{r})\rho(\vec{r}\,')\,v(\vec{r},\vec{r}\,')$$

$$+ E_{xc}[\rho]$$

vary with ρ

$$\frac{\delta T}{\delta \rho} + \frac{\delta E_{xc}}{\delta \rho} + \int d\vec{r}\,'\rho(\vec{r}\,')\,v(\vec{r},\vec{r}\,')$$

$$+ \frac{\delta E_{xc}}{\delta \rho} = \lambda \rho(\vec{r})$$

$$v_{eff}(\vec{r}) = v_{ext}(\vec{r}) + \frac{\delta E_{xc}}{\delta \rho} = V_{xc}$$

$$+ \int d\vec{r}\,'\rho(\vec{r}\,')\,v(\vec{r},\vec{r}\,')$$

can define an effective sp-equation

$$\left[t(\vec{r}) + v_{eff}(\vec{r}) \right] \psi_k^{KS}(\vec{r})$$

$$= \varepsilon_k^{KS} \psi_k^{KS}$$

$$V_{xc}[\rho] = \frac{\delta E_{xc}}{\delta \rho} = V_{xc}[\rho(\vec{r}), \nabla\rho(\vec{r}),$$

$\vec{\partial}(\vec{\partial}\rho(\vec{r}))\ldots]$

Local density approx

$$V_{xc}[\rho](\vec{r}) = V_{xc}(\rho(\vec{r}))$$

$$E_{xc} \stackrel{\sim}{=} \int d\vec{r}\, \varepsilon_{xc}[\rho(\vec{r})]\,\rho(\vec{r})$$

$$\varepsilon_{xc}[\rho] = -\text{const}\,\rho^{1/3}(\vec{r})$$

(From homogeneous el gas)

$$E_{xc} = -\text{const}\int d\vec{r}\,\rho^{4/3}$$

$$V_{xc} = \frac{\delta E_{xc}}{\delta \rho} = -\,4/3 \cdot \text{const} \times \rho^{1/3}$$

$$= -\,\text{const}\, \rho^{1/3}$$

$$\Big[\, t(\vec{r}) + v_{ext}(\vec{r}) + \int d\vec{r}\,'\rho(\vec{r}\,') \times v(\vec{r},\vec{r}\,')$$

$$-\,\text{const}\, \rho^{1/3}(\vec{r})\Big]\, \psi_K(\vec{r})$$

$$= \varepsilon_K^{KS}\, \psi_K(\vec{r})$$