FYS4480/9480 October 17

DFT: $E[n] = ?$

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{int} + H_{II}$$

$$\hat{V}_{ext} = \sum_{i=1}^{N} v_{ext}(x_i)$$

$$x_i = \{\vec{r}_i, \sigma_i\}$$

$$\hat{V}_{int} = \sum_{i<j} v(x_{ij})$$

$$x_{ij} = |x_i - x_j|$$

$$\hat{T} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m} \nabla_i^2$$

$$E[n] = T[n] + V_{ext}[n] + V_{int}[n] + \cancel{E_{II}}$$

$$\langle \hat{V}_{ext} \rangle = \langle \Phi | \sum_{i=1}^{N} v_{ext}(x_i) | \Phi \rangle$$

$$= \int dx_1\, dx_2 \ldots dx_N\, \Phi^*(x_1, x_2 \ldots x_N) \sum_{i=1}^{N} v_{ext}(x_i)\, \Phi(x_1, x_2, \ldots x_N)$$

$$n(x) = \langle \Phi | \hat{n}(x) | \Phi \rangle$$

$$= N \int dx_2 \ldots dx_N\, |\Phi(x_1 x_2 \ldots x_N)|^2$$

$$\hat{n}(x) = \sum_{i=1}^{N} \delta(x - x_i)$$

$$\int dx\, n(x) = N$$

$$\langle \Phi | V_{ext} | \Phi \rangle =$$

$$\int dx_1 \int dx_2 \cdots \int dx_N \, |\Phi(x_1 \cdots x_N)|^2$$
$$\left(v_{ext}(x_1) + v_{ext}(x_2) + \cdots + v_{ext}(x_N) \right)$$

$$= \int dx_1\, v_{ext}(x_1) \int dx_2 \cdots \int dx_N \, |\Phi|^2$$

$$+ \int dx_1 \int dx_2\, v_{ext}(x_2) \int dx_3 \cdots \int dx_N$$
$$\times |\Phi|^2 + \cdots$$

$$\int dx_1 \cdots \int dx_N\, v_{ext}\, |\Phi|^2$$

$$= N \int dx\, v_{ext}(x) \int dx_2 \cdots dx_N$$

$$\times \left| \Phi(x, x_2 \cdots x_N) \right|^2$$

$$= \int dx\, v_{ext}(x)\, n(x)$$

$$= V_{ext}[n]$$

$$V_{int}[n]$$

$$N = 2$$

$$\int dx_1\, dx_2\, \Phi^*(x_1, x_2) \frac{1}{|x_1 - x_2|} \Phi(x_1, x_2)$$

$$= \int dx_1 \int dx_2 \, \frac{|\Phi(x_1 x_2)|^2}{|x_1 - x_2|}$$

$N = 3$

$$\int dx_1 \, dx_2 \, dx_3 \, \frac{\Phi^*(x_1, x_2 x_3) \, \Phi(x_1, x_2 x_3)}{|x_1 - x_2|}$$

$$+ \int dx_1 \, dx_2 \, dx_3 \, \frac{|\Phi(x_1 x_2 x_3)|^2}{|x_1 - x_3|}$$

$$+ \int dx_1 \, dx_2 \, dx_3 \, \frac{|\Phi(x_1 x_2 x_3)|^2}{x_2 - x_3}$$

Define

$$\rho_2(x_1, x_2) = \int dx_3 \, |\Phi|^2$$

$$\rho_2(x_1, x_3) = \int dx_2 \, |\Phi|^2$$

$$\rho_2(x_2 \, x_3) = \int dx_1 \, |\Phi|^2$$

$\Rightarrow$

$$\int dx_1 \, dx_2 \, \frac{\rho_2(x_1 \, x_2)}{|x_1 - x_2|}$$

$$+ \int dx_1 \, dx_3 \, \frac{\rho_2(x_1 \, x_3)}{|x_1 - x_3|} + \int dx_2 \, dx_3 \, \frac{\rho_2(x_2 x_3)}{|x_2 - x_3|}$$

general

$$\Rightarrow \quad \frac{N(N-1)}{2} \int dx\, dx' \frac{\rho_2(x,x')}{|x-x'|}$$

$$N(N-1)\rho_2(x,x') = N^2 n(x)\, n'(x')$$

$$\left(n(x)\, n(x') \right)$$

$$- N\delta(x-x')\, n'(x)$$

or just

$$\int dx\, dx' \frac{n(x)\, n(x')}{|x-x'|}$$

$$\Phi_0 = \frac{1}{\sqrt{N}} \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \cdots & \varphi_1(x_N) \\ \varphi_2(x_1) & & & \vdots \\ \vdots & & & \vdots \\ \varphi_N(x_1) & & & \varphi_N(x_N) \end{vmatrix}$$

$$n(x_1) = N \int dx_2\, dx_3 \cdots dx_N \; |\Phi_0(x_1 x_2 \cdots x_N)|^2$$

$$= \sum_{i=1}^{N} |\varphi_i(x_1)|^2$$

$$x_1 \to x \quad \Rightarrow \quad n(x) = \sum_{i=1}^{N} |\varphi_i(x)|^2$$

For fermions and an SD ansatz

$$V_{int}[n] = \int dx\, dx' \frac{n(x)\, n(x')}{|x - x'|}$$

$$\left\{ \overbrace{\frac{1}{2} \sum_{ij} \langle ij | w | ij \rangle}^{\text{Hartree term (Direct)}} \right\}$$

$$E_{xc}[n]$$

$$E_{HK}[n] = T[n] + V_{ext}[n]$$

$$+ \int dx\,dx' \frac{n(x)\,n(x')}{|x-x'|}$$

$$+ E_{xc}[n]$$

Simple - model : Thomas-Fermi-Dirac

$T[n]$ replaced by electron gas

$$\downarrow$$

$$C_1 \int d\vec{r}\, n(\vec{r})^{5/3} \qquad C_1 = \frac{3}{10}(3\pi^2)^{2/3}$$

$$V_{ext}[n] = \int d\vec{r}\, v_{ext}(\vec{r})\, n(\vec{r})$$

we will also have

$$\frac{1}{2}\int d\vec{r}\int d\vec{r}\,'\, \frac{n(\vec{r})\, n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

$$\int d\vec{r}\, n(\vec{r}) = N$$

$$E_{xc}[n] = c_2 \int d\vec{r}\, n(\vec{r})^{4/3}$$

$$c_2 = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

Variational calculus wrt $n(\vec{r})$ to find equations of motion