Problem Set 2 "Foundations of DFT"

Problem 3 Thomas-Fermi model

$$\varphi_{\vec{k}\sigma}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}}$$

a) $$n(\vec{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{\substack{\vec{k} \\ |\vec{k}|\leq k_F}} |\varphi_{\vec{k}\sigma}(\vec{r})|^2$$

$$= 2 \frac{1}{V} \sum_{\substack{\vec{k} \\ |\vec{k}|\leq k_F}} 1 = 2 \int_{|\vec{k}|\leq k_F} \frac{d^3k}{(2\pi)^3}$$

$$= 2 \frac{1}{(2\pi)^3} 4\pi \int_0^{k_F} dk\, k^2 = \frac{k_F^3}{(3\pi)^2}$$

$$\rightsquigarrow k_F = (3\pi^2 n)^{1/3}$$

b) $$t_s(n) = \frac{1}{V} \langle \Phi | \hat{T} | \Phi \rangle$$

where Φ is Slater-determinant with plane waves occupied for $|\vec{k}| \leq k_F$

$$t_s(n) = \frac{1}{V} \sum_\sigma \sum_{\substack{\vec{k} \\ |\vec{k}|\leq k_F}} \int d^3r\, \varphi^*_{\vec{k}\sigma}(\vec{r}) \left(-\frac{\vec{\nabla}^2}{2}\right) \varphi_{\vec{k}\sigma}(\vec{r})$$

$$= \frac{1}{V} \sum_\sigma \sum_{\substack{\vec{k} \\ |\vec{k}|\leq k_F}} \frac{k^2}{2} = \int_{|\vec{k}|\leq k_F} \frac{d^3k}{(2\pi)^3} k^2$$

$$= \frac{1}{2\pi^2} \int_0^{k_F} dk\, k^4 = \frac{k_F^5}{10\pi^2} = \frac{(3\pi^2)^{5/3}}{10\pi^2} n^{5/3}$$

c) $$E^{TF}[n] = T_s^{TF}[n] + \int d^3r\, v_0(\vec{r})\, n(\vec{r}) + \underbrace{\frac{1}{2}\int d^3r \int d^3r' \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r}-\vec{r}'|}}_{U[n]}$$

$$T_s^{TF}[n] = C^{TF} \int d^3r\, (n(\vec{r}))^{5/3} \qquad C^{TF} = \frac{(3\pi^2)^{5/3}}{10\pi^2}$$

use method of Lagrange multipliers to incorporate constraint that $\int d^3r\, n(\vec{r}) = N$

↳ TF equation from

$$\frac{\delta}{\delta n(\vec{r})} \left[E^{TF}[n] - \mu \left(\int d^3r\, n(\vec{r}) - N \right) \right] = 0$$

$$\frac{\delta}{\delta n(\vec{r})} T_s^{TF}[n] = \frac{5}{3} C^{TF} (n(\vec{r}))^{2/3}$$

$$\frac{\delta}{\delta n(\vec{r})} \int d^3r'\, v_0(\vec{r}')\, n(\vec{r}') = v_0(\vec{r})$$

$$\frac{\delta}{\delta n(\vec{r})} U[n] = \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} = v_H(\vec{r})$$

↳ TF equation

$$\boxed{\frac{5}{3} C^{TF} (n(\vec{r}))^{2/3} + v_0(\vec{r}) + v_H(\vec{r}) - \mu = 0}$$

Problem 4 Hartree-Fock equations

$$E^{HF}[\{\varphi_{n\sigma}\}] = \sum_\sigma \sum_n \int d^3r\, \varphi^*_{n\sigma}(\vec{r}) \left(-\frac{\nabla^2}{2}\right) \varphi_{n\sigma}(\vec{r})$$

$$+ \int d^3r\, v(\vec{r})\, n(\vec{r}) + U[n] + E_x[\{\varphi_{n\sigma}\}]$$

with $$U[n] = \frac{1}{2}\int d^3r \int d^3r' \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r}-\vec{r}'|}$$ Hartree energy

$$E_x[\{\varphi_{n\sigma}\}] = -\frac{1}{2}\sum_{\sigma}\int d^3r \int d^3r' \frac{|\rho_\sigma(\vec{r},\vec{r}')|^2}{|\vec{r}-\vec{r}'|}$$ exchange energy

$$\rho_\sigma(\vec{r},\vec{r}') = \sum_{n=1}^{N_\sigma} \varphi^*_{n\sigma}(\vec{r})\, \varphi_{n\sigma}(\vec{r}')$$

$$n(\vec{r}) = \sum_\sigma \rho_\sigma(\vec{r},\vec{r}) = \sum_\sigma \sum_{n=1}^{N_\sigma} |\varphi_{n\sigma}(\vec{r})|^2$$

$$\frac{\delta}{\delta\varphi^*_{j\sigma}(\vec{r})} \sum_{\sigma'}\sum_n \int d^3r'\, \varphi^*_{n\sigma'}(\vec{r}') \left(-\frac{\nabla^2}{2}\right) \varphi_{n\sigma'}(\vec{r}') = -\frac{\nabla^2}{2}\varphi_{j\sigma}(\vec{r})$$

$$\frac{\delta}{\delta\varphi^*_{j\sigma}(\vec{r})} \int d^3r'\, v(\vec{r}')\, n(\vec{r}') = \int d^3x \underbrace{\left(\frac{\delta}{\delta n(\vec{x})}\int d^3r'\, v(\vec{r}')\, n(\vec{r}')\right)}_{v(\vec{x})} \underbrace{\frac{\delta n(\vec{x})}{\delta\varphi^*_{j\sigma}(\vec{r})}}_{\varphi_{j\sigma}(\vec{r})\delta(\vec{r}-\vec{x})}$$

$$= v(\vec{r})\, \varphi_{j\sigma}(\vec{r})$$

$$\frac{\delta}{\delta\varphi^*_{j\sigma}(\vec{r})} U[n] = \int d^3x \underbrace{\left(\frac{\delta}{\delta n(\vec{x})} U[n]\right)}_{v_H(\vec{x}) = \int dr' \frac{n(\vec{r}')}{|\vec{x}-\vec{r}'|}} \frac{\delta n(\vec{x})}{\delta\varphi_{j\sigma}(\vec{r})} = v_H(\vec{r})\, \varphi_{j\sigma}(\vec{r})$$

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$$\frac{\delta}{\delta \varphi^*_{j\sigma}(\vec r)} E_x[\{\varphi_{k\sigma}\}]$$

$$= \int d^3x \int d^3x' \left[\underbrace{\left(\frac{\delta}{\delta \rho^*_\sigma(\vec x \vec x')} E_x\right)}_{-\frac{1}{2}\frac{\overbrace{\rho_\sigma(\vec x \vec x')}^{\rho^*_\sigma(\vec r,\vec x)}}{|\vec x - \vec x'|}} \underbrace{\frac{\delta \rho^*_\sigma(\vec x \vec x')}{\delta \varphi^*_{j\sigma}(\vec r)}}_{\varphi_{j\sigma}(\vec x)\,\delta(\vec x' - \vec r)} + \underbrace{\left(\frac{\delta E_x}{\delta \rho_\sigma(\vec x \vec x')}\right)}_{-\frac{1}{2}\frac{\rho^*_\sigma(\vec x \vec x')}{|\vec x - \vec x'|}} \underbrace{\frac{\delta \rho_\sigma(\vec x \vec x')}{\delta \varphi^*_{j\sigma}(\vec r)}}_{\varphi_{j\sigma}(\vec x')\,\delta(\vec x - \vec r)} \right]$$

$$= -\frac{1}{2}\int d^3x \frac{\rho_\sigma(\vec x \vec r)}{|\vec x - \vec r|} \varphi_{j\sigma}(\vec x)$$

$$-\frac{1}{2}\int d^3x' \frac{\rho^*_\sigma(\vec r, \vec x')}{|\vec r - \vec x'|} \varphi_{j\sigma}(x') = -\int d^3x \frac{\rho^*_\sigma(\vec r \vec x)}{|\vec r - \vec x|} \varphi_{j\sigma}(\vec x)$$

$$\frac{\delta}{\delta \varphi^*_{j\sigma}(\vec r)} \left[E^{HF}[\{\varphi_{k\sigma'}\}] - \sum_{\sigma'} \sum_{k'=1}^{N_{\sigma'}} \varepsilon_{k\sigma'} \left(\int d^3r' \, |\varphi_{k\sigma'}(\vec r')|^2 - 1 \right) \right] = 0$$

$$\hookrightarrow \boxed{\left(-\frac{\nabla^2}{2} + v(\vec r) + v_H(\vec r)\right) \varphi_{j\sigma}(\vec r) - \int d^3x \frac{\rho^*_\sigma(\vec r, \vec x)}{|\vec r - \vec x|} \varphi_{j\sigma}(\vec x) = \varepsilon_{j\sigma} \varphi_{j\sigma}(\vec r)}$$

HF equations

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