Electron gas in 3 dims

- uniform distribution of ion charge, positive background charge
- N electrons in a cubic box with L-side, and volume $V = L^3$ and density $\rho = N/L^3$

HF equations in coordinate space

kinetic energy $t(x) = -\frac{\hbar^2 \nabla^2}{2m}$

$$\left(t(x) + u(x) + u_1^{HF} \right) \varphi_\alpha(x)$$

$$+ \int dx' \, u_2^{HF}(x,x') \, \varphi_\alpha(x')$$

$$u_1^{HF}(x) = u^{HARTREE} = \sum_{\alpha' \leq F} \int dx' \, |\varphi_{\alpha'}(x')|^2 \times v(x, x')$$

$$u_2^{HF}(x) = u^{FOCK} = -\sum_{\alpha' \leq F} \varphi_{\alpha'}(x') \, v(x, x') \times \varphi_{\alpha'}(x)$$

$$\varphi_\alpha(x) = \psi_k(\vec{r}) \, \chi_\sigma(\xi) \qquad \sigma = 1/2$$

$$\chi(\xi) = \begin{cases} \begin{bmatrix} 1 \\ 0 \end{bmatrix} & \xi = \uparrow \ (+1/2) \\ \begin{bmatrix} 0 \\ 1 \end{bmatrix} & \xi = \downarrow \ (-1/2) \end{cases}$$

$$v(x, x') = v(|\vec{r} - \vec{r}\,'|), \text{ no spin dependence}$$

$$\sum_{\alpha \le \alpha_F} = \sum_{\xi = +1/2, -1/2} \sum_{k \le k_F}$$

HF - equation

$$\Bigg[-\frac{\hbar^2 \nabla^2}{2m} + u(\vec{r})$$

$$+ 2 \sum_{k' \le k_F} \int d\vec{r}\,' \, |\psi_{k'}(\vec{r}\,')|^2$$

$$v(|\vec{r} - \vec{r}\,'|) \Bigg] \psi_k(\vec{r})$$

$$- \sum_{k' \le k_F} \psi_{k'}(\vec{r}) \int d\vec{r}\,' \psi^*_{k'}(\vec{r}\,') \psi_k(\vec{r}\,') \times v(|\vec{r} - \vec{r}\,'|) \Bigg] =$$

$$\sum_{\sigma_1,\sigma_2} \int d\vec{r}_1 d\vec{r}_2 \; \varphi^*_{\alpha_1}(\vec{r}_1) \boxed{\chi^*(\sigma_1)} \; \varphi^*_{\alpha_2}(\vec{r}_2)\chi(\sigma_2)$$

$[1 \; 0]$

$$v(|\vec{r}_1-\vec{r}_2|) \; \varphi_{\alpha_1}(\vec{r}_1) \boxed{\chi(\sigma_1)}$$

$[0 \; 1]$

$$\times \; \varphi_{\alpha_2}(\vec{r}_2) \, \chi(\sigma_2)$$

$\sigma_1 = +1/2, -1/2$

Hartree term

part 1

$$\begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = 1$$

$\uparrow\uparrow$

$\downarrow\downarrow$

$$\begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = 1$$

$$- \sum_{\sigma_1\sigma_2} \int d\vec{r}_1 d\vec{r}_2 \; \varphi^*_{\alpha_1}(\vec{r}_1) \chi^*(\sigma_1) \; \varphi^*_{\alpha_2}(\vec{r}_2) \chi^*(\sigma_2)$$

$$v(|\vec{r}_1-\vec{r}_2|) \; \underbrace{\varphi_{\alpha_1}(\vec{r}_2) \chi(\sigma_2)}_{\text{part 1}} \; \varphi_{\alpha_2}(\vec{r}_1) \chi(\sigma_1)$$

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

$$u(\vec{r}) = -e \int \frac{\rho(\vec{r}\,')\, d\vec{r}\,'}{|\vec{r}-\vec{r}\,'|}$$

$$\rho(\vec{r}) = [N/V]\, e$$

$$u(\vec{r}) = -\frac{N}{V} e^2 \int \frac{d\vec{r}\,'}{|\vec{r}-\vec{r}\,'|}$$

HF - eigenfunctions and energies

(i) no interaction

$$-\frac{\hbar^2 \nabla^2}{2m} \psi_k(\vec{r}) = \varepsilon_k^{(0)} \psi_k(\vec{r})$$

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

$$\vec{k} = \frac{2\pi}{L}\left[n_{kx}\vec{e}_x + n_{ky}\vec{e}_y + n_{kz}\vec{e}_z\right]$$

$n_k = 0, \pm 1, \pm 2, \ldots$

$$\varepsilon_k^{(0)} = \hbar^2 k^2 / 2m$$

(ii) add $u(\vec{r})$ and $v(\vec{r}, \vec{r}')$

$v(\vec{r}, \vec{r}')$ is translationally invariant and in an infinite system, $\psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}}$ are eigenstates for HF of the interacting. But $\varepsilon_k^{(0)}$ is not an eigenvalue of the Hartree-Fock Hamiltonian.

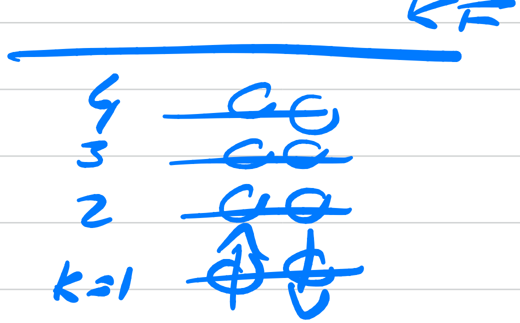
Solving the HF equations,
Hartree-term first

$$2 \sum_{k' \le k_F} \int d\vec{r}' \, |\psi_{k'}(\vec{r}')|^2 \, v(\vec{r}, \vec{r}')$$

$$\psi_{k'}(\vec{r}') = \frac{e^{i\vec{k}'\vec{r}'}}{\sqrt{V}}$$

$$= \frac{2}{V} \sum_{k' \le k_F} \int d\vec{r}' \, \frac{e^2}{|\vec{r} - \vec{r}'|}$$

sums over particles



$$= + \frac{N}{V} \int \frac{d\vec{r} \, e^2}{|\vec{r} - \vec{r}'|} = -u(\vec{r})$$

from ions

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{V^2} \sum_{k' \leq k_F}$$

$$\times \int d\vec{r}\, e^{i(\vec{k}'-\vec{k})\vec{r}} \int d\vec{r}\,' \frac{e^{i(\vec{k}-\vec{k}')\vec{r}\,'}}{|\vec{r}-\vec{r}\,'|}$$

introduce a convergence factor $e^{-\mu|\vec{r}-\vec{r}\,'|}$, $\lim_{\mu \to 0}$

$$\frac{1}{V}\sum_k \to \frac{1}{(2\pi)^3}\int d\vec{k}$$

$$\frac{e^2}{V^2}\sum_{\vec{k}'}\int d\vec{r}\, e^{i(\vec{k}'-\vec{k})\vec{r}}\int d\vec{r}'\frac{e^{i(\vec{k}-\vec{k}')\vec{r}'}}{|\vec{r}-\vec{r}'|}$$

$$= \frac{e^2}{V(2\pi)^3}\int d\vec{r}\int \frac{d\vec{r}}{|\vec{r}-\vec{r}'|}\, e^{-ik(\vec{r}-\vec{r}')}$$

$$\times \int dk' e^{ik'(\vec{r}-\vec{r}')}$$

$$= \lim_{\mu\to 0} \frac{e^2}{V(2\pi)^3}\int d\vec{r}\, d\vec{r}'\, d\vec{k}'\, e^{i(\vec{k}'-\vec{k})(\vec{r}-\vec{r}')}\, \frac{e^{-\mu|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}$$

$$\vec{x} = \vec{r} - \vec{r}\,' \qquad \vec{y} = \vec{r}\,'$$

$$= \lim_{\mu \to 0} \frac{e^2}{V(2\pi)^3} \int d\vec{k} \int d\vec{y}\,' \int d\vec{x}\, e^{i(\vec{k}\,' - \vec{k})\vec{x}} \times \frac{e^{-\mu|\vec{x}|}}{|\vec{x}|}$$

$$\int d\vec{x}\, e^{i(\vec{k}\,' - \vec{k})x} \frac{e^{-\mu|\vec{x}|}}{|\vec{x}|}$$

$$= \int x^2 dx \underbrace{d\Omega}_{\iint d\phi \sin\theta d\theta} e^{i|\vec{k}\,' - \vec{k}||\vec{x}|\cos\theta} \times \frac{e^{-\mu|\vec{x}|}}{|\vec{x}|}$$

$$(|\vec{x}| = x)$$

$$= 2\pi \int x^2 dx \, \frac{e^{-\mu x}}{x} \int_0^{\pi} d\theta \sin\theta$$

$$\times \, e^{i|\vec{k}' - \vec{k}| x \cos\theta}$$

$$= 2\pi \int x^2 dx \, \frac{e^{-\mu x}}{x} \int_{-1}^{1} dy \, e^{i|\vec{k}' - \vec{k}'| x y}$$

$$d\theta \sin\theta = dy$$

$$y = \cos\theta$$

$$= 2\pi \int dx \, \cancel{\frac{x^2}{x^2}} \cdot \frac{2 \sin(|\vec{k}' - \vec{k}| x)\, e^{-\mu x}}{|\vec{k}' - \vec{k}|}$$

$$= \frac{4\pi}{\mu^2 + |\vec{k}' - \vec{k}|^2}$$

$$\Rightarrow \lim_{\mu \to 0} \frac{e^2}{V(2\pi)^3} \int_0^{k_F} d\vec{k}' \underbrace{\int dq'}_{V} \frac{4\pi}{\mu^2 + |\vec{k}' - \vec{k}|^2}$$

$$= \lim_{\mu \to 0} \frac{e^2}{2\pi^2} \int d\vec{k}' \frac{1}{\mu^2 + |\vec{k}' - \vec{k}|^2}$$

$$= \frac{e^2}{2\pi^2} \int_0^{\vec{k}_F} \frac{d\vec{k}'}{|\vec{k}' - \vec{k}|}$$

$$= \frac{e^2}{2\pi^2} \int_0^{k_F} k^2 dk \int 2\pi \, d\theta \sin\theta$$

$$\times \frac{1}{\left[\sqrt{(k'^2 + k^2 - 2|\vec{k}||\vec{k}'| \cos\theta)}\right]^2}$$

$$= \frac{e^2}{\pi} \int_0^{k_F} k'^2 dk' \int_0^{\pi} d\theta \sin\theta \frac{1}{k'^2 + k^2 - 2kk'\cos\theta}$$

$$\cos\theta = u$$

$$= \frac{e^2}{\pi} \int_0^{k_F} k'^2 dk' \int_{-1}^{1} du \frac{1}{k'^2 + k^2 - 2k'ku}$$

$$= \frac{e^2}{\pi} \int_0^{k_F} k' dk' \left\{ \ln|k'+k| - \ln|k'-k| \right\}$$

$$\int_a^b x \ln x = \frac{1}{2} x^2 \ln x \Big|_a^b - \frac{1}{2} \int_a^b x \, dx$$

$$\Rightarrow$$

$$\frac{e^2}{\pi k} \left\{ \frac{k_F^2 - k^2}{2} \ln \left| \frac{k_F + k}{k_F - k} \right| + k k_F \right\}$$

$$\Rightarrow$$

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{\pi k} \left\{ \frac{k_F^2 - k^2}{2} \times \ln \frac{|k_F + k|}{|k_F - k|} + k k_F \right\}$$