

Hartree-Fock - Homogeneous Electron Gas

Exact solutions: $\psi_i(r) = \frac{e^{i\mathbf{k}_i \cdot \mathbf{r}}}{\sqrt{V}} s_i$ $s_i \begin{cases} \alpha \\ \beta \end{cases}$

Coulomb interactions for electrons + positive background cancel.

So we have:

$$\frac{\hbar^2}{2m} \nabla^2 \psi_i(r) - \sum_j \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \psi_j^*(r') \psi_i(r') \psi_j(r) \delta_{s_i s_j} = \epsilon_i \psi_i(r)$$

Plug in above. and use:

$$\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} = \frac{4\pi e^2}{V} \sum_{\mathbf{g}} \frac{1}{g^2} e^{i\mathbf{g} \cdot (\mathbf{r}-\mathbf{r}')} = 4\pi e^2 \int \frac{d\mathbf{g}}{(2\pi)^3} \frac{1}{g^2} e^{i\mathbf{g} \cdot (\mathbf{r}-\mathbf{r}')}$$

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi} k_F F\left(\frac{k}{k_F}\right)$$

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$$

$$E = 2 \sum_{k < k_F} \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{\pi} \sum_{k < k_F} \left[1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right]$$

$$= N \left[\frac{3}{5} \epsilon_F - \frac{3}{4} \frac{e^2 k_F}{\pi} \right] \quad \epsilon_F = \frac{\hbar^2 k_F^2}{2m}$$

$$\frac{E}{N} = \frac{3}{5} \epsilon_F - \frac{3}{4} \frac{e^2 k_F}{\pi}$$

in atomic (Rydberg) units:

$$\frac{E}{N} = \frac{3}{5} k_F^2 - \frac{3}{2\pi} k_F = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} \quad \text{Ryd}$$

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

$$n = \frac{N}{V}$$

$$k_F = \frac{(9\pi/4)^{1/3}}{r_s} = \frac{1.92}{r_s}$$

Exact leading terms for small r_s (high density)

$$\frac{E}{N} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.0622 \ln(r_s) - 0.091 + O(r_s)$$

not really
small
though!

$$r_s = 2-6 \quad \rho = 0$$

Note that the average exchange energy:

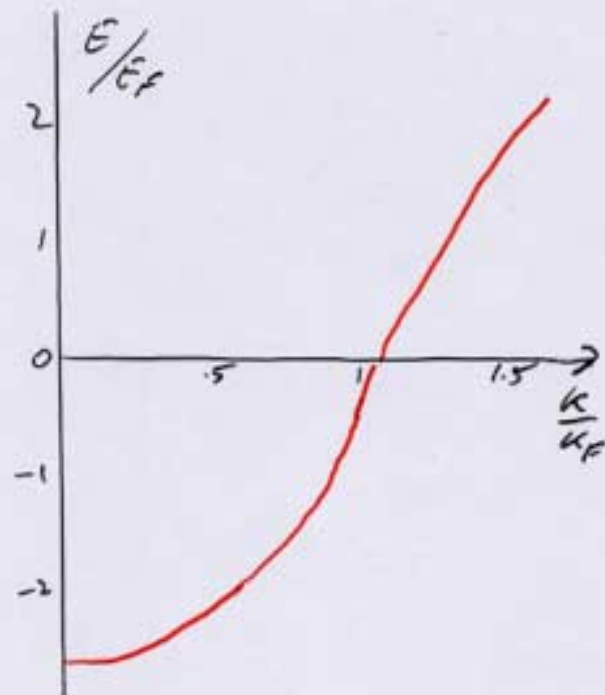
$$-\frac{3}{4} \frac{e^2 k_F}{\pi} = -\frac{0.916}{r_s} \text{ Ryd}$$

$$E_x \propto \frac{1}{r_s} \propto n(r)^{1/3}$$

Local density exchange

$$\text{Slater exchange: } -2.95 n(r)^{1/3}$$

HF electron gas



Fermi velocity $\frac{dE}{dk} \rightarrow \infty$!!

DOS $N(E_F) \rightarrow 0$

Need screening!

HF cannot be used for metals!!