$$H\psi = \left(\sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0}\sum_R \frac{1}{|r_i - R|}\right)\psi$$
$$+ \frac{1}{2}\sum_{i\neq j} \frac{e^2/4\pi\varepsilon_0}{|r_i - r_j|}\psi = E\psi$$

<u>Hartree</u>: avg. potential or just product wavefnt.

$$U^{ion} = -\frac{Ze^2}{4\pi\varepsilon_0}\sum_R \frac{1}{|r-R|}$$
$$U^{el} = \frac{e^2}{4\pi\varepsilon_0}\sum_j \int d^3r' \, |\psi_j(r')|^2 \frac{1}{|r-r'|}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i + (U^{ion} + U^{el})\psi_i = \varepsilon_i\psi_i$$

Solved self-consistently.

Misses exchange, antisymmetric wavefunction.

<u>Hartree-Fock</u>: $\psi(r_1 s_1, r_2 s_2, \dots) = \begin{vmatrix} \psi_1(r_1 s_1) & \psi_1(r_2 s_2) & \dots & \psi_1(r_N s_N) \\ \psi_2(\;''\;) & & & \\ \vdots & & & \\ \psi_N(\;''\;) & & & \end{vmatrix}$

(Hartree just 1 column.)

Minimize: $\langle H\rangle_\psi = \dfrac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$.

Result:

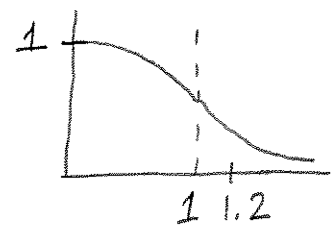
$$-\frac{\hbar^2}{2m}\nabla^2\psi_i + (U^{ion} + U^{el})\psi_i$$
$$-\sum_j \int d^3r' \frac{e^2}{4\pi\varepsilon_0|r-r'|}\psi_j^*(r')\psi_i(r')\psi_j(r)\delta_{s_i s_j} = \varepsilon_i\psi_i$$

Free electron soln. HF

$$\psi_i = \frac{e^{i k_i \cdot r}}{\sqrt{\mathrm{Vol}}} \times \text{spinor}$$

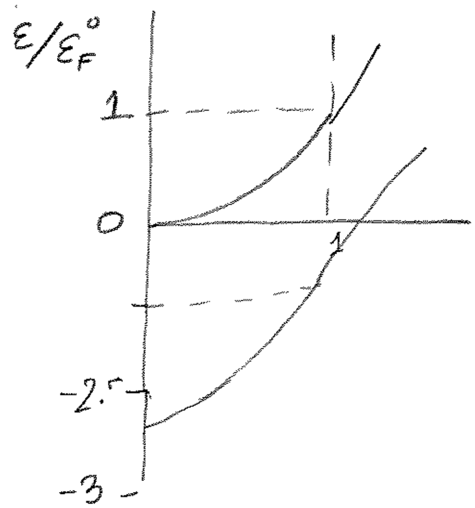
$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{(4\pi\varepsilon_0)\pi} k_F F\left(\frac{k}{k_F}\right)$$

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



$\frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k}$ log div.

(see screening)



Sum over all energies of occ. states:

$$E = N\left(\frac{3}{5}\varepsilon_F - \frac{3}{4}\frac{e^2 k_F}{4\pi\varepsilon_0 \pi}\right)$$

$$\frac{e^2}{4\pi\varepsilon_0 2a_0} = 1\,Ry$$

$$\frac{E}{N} = \frac{e^2}{2a_0}\left[\frac{3}{5}(k_F a_0)^2 - \frac{3}{2\pi}(k_F a_0)\right]$$

Remember r_s: $(r_s/a_0 = 2 \text{ to } 6)$ $\quad \frac{1}{n} = \frac{4\pi r_s^3}{3}$

sim. size

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

$$+ \; 0.0622 \ln(r_s/a_0) - 0.096 + \mathcal{O}(r_s/a_0)$$

exact

Screening:

$$-\nabla^2 \phi^{ext} = \rho^{ext}/\varepsilon_0$$

$$-\nabla^2 \phi = \rho/\varepsilon_0$$

$$\rho = \rho^{ext} + \rho^{ind}$$

$$\rho^{ind}(q) = \chi(q)\phi(q)$$

$$q^2 \phi^{ext} = \rho^{ext}/\varepsilon_0$$

$$q^2 \phi = \rho(q)/\varepsilon_0$$

$$\rightarrow \quad q^2(\phi(q) - \phi^{ext}(q)) = \chi(q)\phi(q)/\varepsilon_0$$

$$\left(q^2 - \frac{\chi}{\varepsilon_0}\right)\phi = q^2 \phi_{ext}$$

$$\phi = \frac{\phi_{ext}}{1 - \frac{\chi}{\varepsilon_0 q^2}} = \frac{\phi_{ext}(q)}{\varepsilon(q)}$$

$4\pi\varepsilon_0 = 1$

$\varepsilon_0 = 1/4\pi$

Thomas-Fermi screening

$$n(r) = \int \frac{d^3k}{4\pi^3} \frac{1}{\exp(\beta(\varepsilon_k - e\phi - \mu)) + 1}$$

$$n_0(\mu) = \int \frac{d^3k}{4\pi^3} \frac{1}{\exp(\beta(\varepsilon_k - \mu)) + 1}$$

$$\rho^{ind} = -e\left[n_0(\mu + e\phi) - n_0(\mu)\right]$$

$$\rho^{ind} = -e^2 \frac{\partial n_0}{\partial \mu} \phi \quad \rightarrow \chi = -e^2 \frac{\partial n_0}{\partial \mu}$$

$$\rightarrow \varepsilon(q) = 1 + \frac{e^2}{\varepsilon_0 q^2} \frac{\partial n_0}{\partial \mu} = 1 + \frac{k_0^2}{q^2}$$

$$k_0^2 = \frac{e^2}{\varepsilon_0} \frac{\partial n_0}{\partial \mu}$$

For $\phi^{ext} = \dfrac{Q}{4\pi\varepsilon_0 r}$ $\quad \phi^{ext}(q) = \dfrac{Q}{\varepsilon_0 q^2}$

$$\phi = \frac{1}{\varepsilon(q)} \phi^{ext}(q) = \frac{Q/\varepsilon_0 q^2}{1 + k_0^2/q^2} = \frac{Q}{\varepsilon_0} \frac{1}{q^2 + k_0^2}$$

$$\phi(r) = \int \frac{d^3q}{(2\pi)^3} e^{iq \cdot r} \frac{Q}{\varepsilon_0} \frac{1}{(q^2 + k_0^2)} = \frac{Q}{4\pi\varepsilon_0 r} e^{-k_0 r}$$

(screened coulomb)

For $T \ll T_F$, $\partial n_0 / \partial \mu = g(\varepsilon_F) = \dfrac{m k_F}{\hbar^2 \pi^2}$

$$\frac{k_0^2}{k_F^2} = \frac{4}{\pi(k_F a_0)} \rightarrow k_0 = 0.815\, k_F \left(\frac{r_s}{a_0}\right)^{1/2} \sim k_F$$

atomic scale