FYS4480/9480 lecture Oct 10

Topics this week: the homogeneous electron gas in three dimensions, Hartree-Fock energies and ground state energy

$$\varepsilon_p^{HF} = \langle p|\hat{h}_0|p\rangle + \sum_{j\leq F} \langle pj|\hat{v}|pj\rangle_{AS}$$

two-body interaction

$$\hat{t} + \hat{u}_{ext}$$

kinetic energy

external potential

$$\hat{t} = -\frac{\hbar^2 \nabla^2}{2m}$$

For a particle in a box (3d) with periodic boundary conditions

$$\vec{k} = \frac{2\pi}{L}\left(n_1 \vec{e}_1 + n_2 \vec{e}_2 + n_3 \vec{e}_3\right)$$

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

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

$$\hat{t}\,\varphi_{\vec{k}}(\vec{r}) = \frac{\hbar^2 k^2}{2m} \varphi_{\vec{k}}(\vec{r})$$

$$\langle \vec{p} | \hat{t} | \vec{p} \rangle = \frac{\hbar^2 p^2}{2m} =$$

$$\frac{1}{\Omega} \int_\Omega d\vec{r} \, \frac{\hbar^2 p^2}{2m} \left| \varphi_{\vec{p}}(\vec{r}) \right|^2 = \frac{\hbar^2 p^2}{2m}$$

$p^2 \propto n_1^2 + n_2^2 + n_3^2$, gives rise to "magic" numbers

$m_1^2+m_2^2+m_3^2$	m_1	m_2	m_3		$N_{\uparrow\downarrow}$
0	0	0	0		2
1	-1	0	0	12	
$-1-$	1	0	0		
	0	-1	0		
$-1-$	0	1	0		
	0	0	-1		
$-1-$	0	0	1		14
2	-1	-1	0	24	
	+ 11 more				38
3	-1	-1	-1	16	
	+ 7 more				54

closed shells (magic numbers)

2, 14, 38, 54, 68, 114, ... $N \Rightarrow \infty$

external potential

$$u_{ext}(\vec{r}) = -e \int_\Omega \frac{\rho(\vec{r}\,')\, d\vec{r}\,'}{|\vec{r} - \vec{r}\,'|}$$

$$\rho(\vec{r}\,') = \frac{N}{\Omega} e$$

$N = N_e$

$$u_{ext} = -\frac{N}{\Omega} e^2 \int_\Omega \frac{d\vec{r}\,'}{|r - \vec{r}\,'|}$$

$$\langle p | u^{HF} | p \rangle = \sum_{j \le F} \langle p j | v | p j \rangle - \sum_{j \le F} \langle \overset{(1\ 0)}{\underline{p}}\, j | v | \overset{\binom{0}{1}}{\underline{j}}\, p \rangle$$

$$\sum_{\sigma_j = \pm 1/2} \sum_{j \le k_F} \langle p \sigma_p\, j \sigma_j | v | p \sigma_p\, j \sigma_j \rangle$$

independent of spin

σ_p is fixed

$$(1\ 0)\begin{pmatrix}1\\0\end{pmatrix} \quad \text{and} \quad (0\ 1)\begin{pmatrix}0\\1\end{pmatrix}$$

$$= 2 \sum_{j \le k_F} \langle pj | v | pj \rangle$$

Exchange term :

$$- \sum_{j \le k_F} \langle pj | v | pj \rangle = \int d\vec{r} \int d\vec{r}\,'$$

$$\left(\frac{1}{\sqrt{\Omega}} e^{i\vec{k}\vec{r}} \right)$$

$$= - \frac{e^2}{\Omega^2} \sum_{j \le k_F} \int d\vec{r}\, e^{i(\vec{j}-\vec{p})\vec{r}}$$

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

Direct term

$$\frac{2}{\Omega}\sum_{p\leq k_F}\int_{\Omega} d\vec{r}\,'\frac{e^2}{|\vec{r}-\vec{r}\,'|} \qquad \int_V d\vec{r} = V$$

$$= \frac{N e^2}{\Omega}\int d\vec{r}\,'\frac{1}{|\vec{r}-\vec{r}\,'|} = -u_{ext}(\vec{r})$$

$$\varepsilon_p^{HF} = \frac{\hbar^2 p^2}{2m} - \text{Exchange term}$$

$p \Rightarrow k \qquad q \Rightarrow k'$

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{\Omega^2} \sum_{k' \leq k_F} \int d\vec{r}$$

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

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

How do we evaluate the exchange term.

1) convergence factor $e^{-\mu|\vec{r}-\vec{r}'|}$

Evaluate integral and take limit $\mu \to 0$

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

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

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

new variables

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

$$\lim_{\mu \to 0} \frac{e^2}{\Omega (2\pi)^3} \int d\vec{k}' \int d\vec{y} \int d\vec{x}$$

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

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

$$= \int x^2 dx \int d\theta \sin\theta \, d\varphi$$

$$\times \; e^{i|\vec{k}-\vec{k}||x|\cos\theta} \; \frac{e^{-\mu|\vec{x}|}}{|\vec{x}|}$$

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

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

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

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

$$\lim_{\mu \to 0} \frac{e^2}{\Omega (2\pi)^3} \int_0^{k_F} d\vec{k}' \int d\vec{q} \frac{4\pi}{\mu^2 + |\vec{k}' - \vec{k}|^2}$$

$$\int d\vec{q} = \Omega$$

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

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

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

k' k

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

$$\times \frac{1}{k'^2+k^2-2k'k\cos\theta}$$

$$\cos\theta = u$$

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

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

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

$$x = k/k_F$$

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

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi} F(k/k_F)\, k_F$$

non-interacting energy at the Fermi level

$$\varepsilon_0^F = \frac{\hbar^2 k_F^2}{2m}$$

$$\varepsilon_k^{HF} / \varepsilon_0^F = x^2 - \frac{4 e^2 m}{\hbar^2 k_F \pi} F(x)$$

Bohr radius $\quad a_0 = \dfrac{\hbar^2}{e^2 m}$

$$n = \frac{N}{\Omega} = 2 \int_0^{k_F} k^2 dk \overbrace{\int d\cos\theta \, d\varphi}^{4\pi} \times \frac{1}{(2\pi)^3}$$

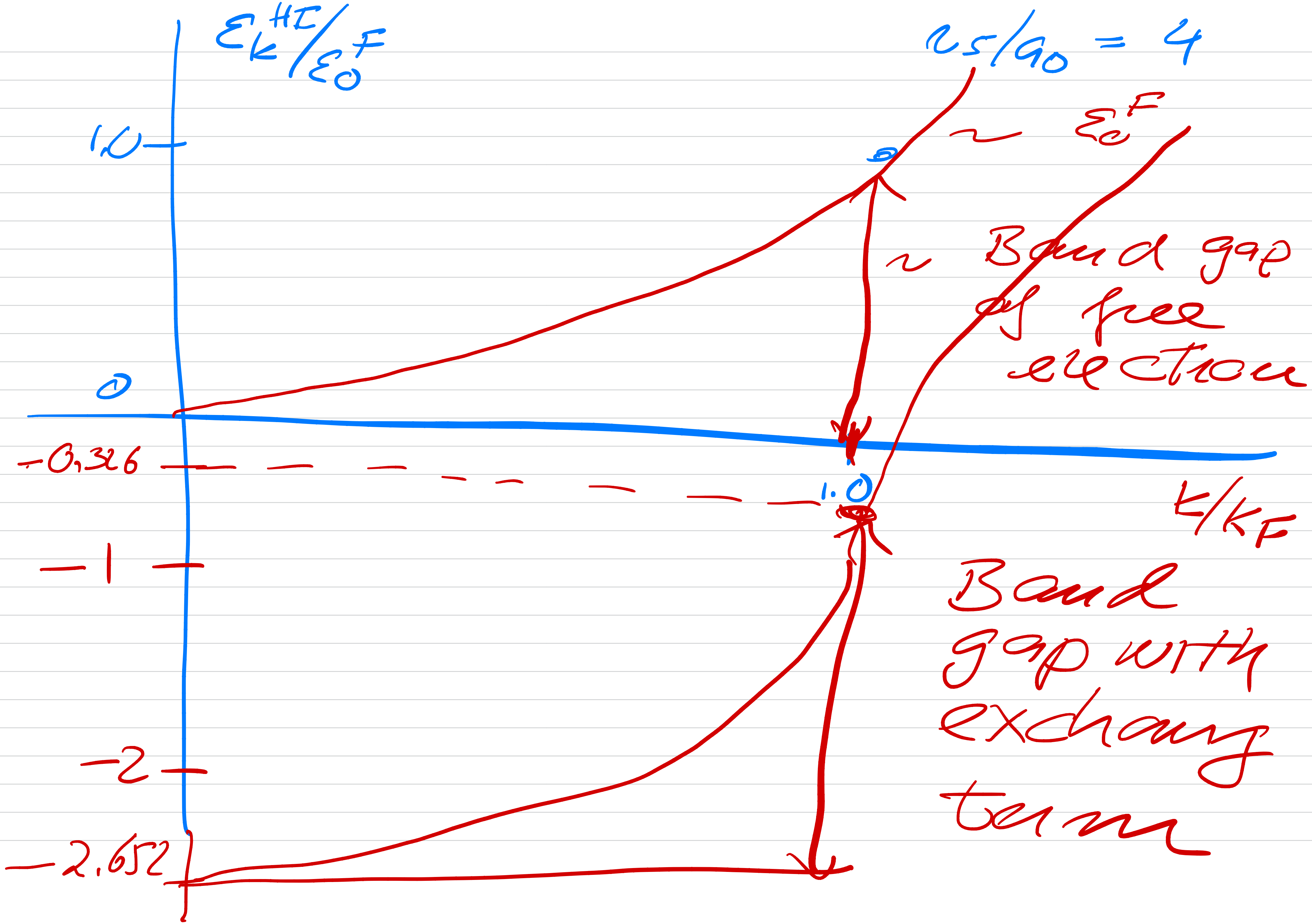
$$= \frac{k_F^3}{3\pi^2} = \frac{N}{\Omega} = \frac{3}{4\pi r_s^3}$$

r_s = radius of a sphere whose volume is the volume per electron

$k_F = 1.92/r_s \implies$

$$\varepsilon_K^{HF}/\varepsilon_0^F = x^2 - \left(\frac{r_s}{a_0}\right) 0.663\, F(x)$$

$r_s/a_0 \sim 2-6$ for most metals



$\varepsilon_k^{HF}/\varepsilon_0^F$
$r_s/a_0 = 4$
1.0
0
-0.326
-1
-2
-2.652
1.0
k/k_F
$\sim \varepsilon_0^F$
$\sim$ Band gap of free electron
Band gap with exchange term

$$\Delta E^{HF} = E^{HF}_{k_F} - E^{HF}_{k=0}$$

$$= 2{,}326$$