PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

Plan for Lecture 12:

Reading: Chap. 4 in GGGPP;

One-electron approximations to the many electron problem

1. **Hartree-Fock approximation**
2. **Density functional theory**

Course schedule

(Preliminary schedule -- subject to frequent adjustment.)

	Date	F&W Reading	Topic	Assignment
1	Wed, 8/26/2015	Chap. 1.1-1.2	Electrons in a periodic one-dimensional potential	#1
2	Fri, 8/28/2015	Chap. 1.3	Electrons in a periodic one-dimensional potential	#2
3	Mon, 8/31/2015	Chap. 1.4	Tight binding models	#3
4	Wed, 9/02/2015	Chap. 1.6, 2.1	Crystal structures	#4
5	Fri, 9/04/2015	Chap. 2	Group theory	#5
6	Mon, 9/07/2015	Chap. 2	Group theory	#6
7	Wed, 9/09/2015	Chap. 2	Group theory	#7
8	Fri, 9/11/2015	Chap. 2	Group theory	#7
9	Mon, 9/14/2015	Chap. 2.4-2.7	Densities of states	#8`
10	Wed, 9/16/2015	Chap. 3	Free electron model	#9
11	Fri, 9/18/2015	Chap. 4	One electron approximations to the many electron problem	#10
12	Mon, 9/21/2015	Chap. 4	One electron approximations to the many electron problem	#11
13	Wed, 9/23/2015			
14	Fri, 9/25/2015			
15	Mon, 9/28/2015			
16	Wed, 9/30/2015			

Quantum Theory of materials

Electronic Schrödinger equation:

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = U_\alpha(\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{a,i}\frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Hartree approximation to electronic wavefunction

$$\Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_1)\phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_2)....\phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_N)$$

$$=\prod_{i=1}^{N}\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}_i)$$

Variational estimate of electron energy in Hartree approximation

$$E_H = \frac{\left\langle \Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\middle| H \middle| \Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle}{\left\langle \Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\middle| \Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle}$$

Let $\mathcal{F}_H \equiv \left\langle \Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\middle| H \middle| \Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle$

and require $\left\langle \phi_{n_i\mathbf{k}_i\sigma_i}\middle|\phi_{n_i\mathbf{k}_i\sigma_i}\right\rangle = 1$, then the variational equations for the Hartree orbitals are:

$$\frac{\partial \mathcal{F}_H}{\partial \phi_{n_i\mathbf{k}_i\sigma_i}^*} = \epsilon_i \phi_{n_i\mathbf{k}_i\sigma_i}$$

Variational equation for Hartree approximation -- continued

$$\frac{\partial \mathcal{F}_H}{\partial \phi_{n_i\mathbf{k}_i\sigma_i}^*} = \epsilon_i \phi_{n_i\mathbf{k}_i\sigma_i}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{Ne}(\mathbf{r}) + V_{ee}(\mathbf{r})\right)\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}) = \epsilon_i \phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r})$$

Nuclear-electron interaction:

$$V_{Ne}(\mathbf{r}) \equiv -\sum_a \frac{Z^a e^2}{|\mathbf{r}-\mathbf{R}^a|}$$

Electron-electron interaction:

$$V_{ee}(\mathbf{r}) \equiv e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

where $n(\mathbf{r}') \equiv \sum_{n_i\mathbf{k}_i\sigma_i} \left|\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}')\right|^2$

Note: In principle, the self interaction term should be omitted from $V_{ee}(r)$, but often it is included.

Hartree approximation -- continued

In practice, the equations must be solved self-consistently

One possible procedure would start with a guess of the one-electron functions $\left\{\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r})\right\}$ and the electron density

where $n(\mathbf{r}') \equiv \sum_{n_i\mathbf{k}_i\sigma_i} \left|\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}')\right|^2$

Next, find new one electron functions from:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{Ne}(\mathbf{r}) + V_{ee}(\mathbf{r})\right)\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}) = \epsilon_i \phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r})$$

and determine the new electron density $n(\mathbf{r})$. At convergence the electron density is stable.

Hartree approximation -- continued

At convergence, the Hartree electronic energy can be computed from one-electron functions $\left\{\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r})\right\}$ and the electron density

where $n(\mathbf{r}') \equiv \sum_{n_i\mathbf{k}_i\sigma_i} \left|\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}')\right|^2$

$$E_H = E_K + E_{Ne} + E_{ee}$$

$$E_K = -\frac{\hbar^2}{2m}\sum_{n_i\mathbf{k}_i\sigma_i}\int d^3r\ \phi_{n_i\mathbf{k}_i\sigma_i}{}^*(\mathbf{r})\nabla^2\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r})$$

$$E_{Ne} = \int d^3r\ V_{Ne}(\mathbf{r})n(\mathbf{r})$$

$$E_{ee} = \frac{e^2}{2}\int d^3r\int d^3r'\ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Hartree-Fock approximation to electronic wavefunction

Fermi symmetry

$$\Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i...\mathbf{r}_k\},\{\mathbf{R}^a\}) = -\Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_k...\mathbf{r}_i\},\{\mathbf{R}^a\})$$

$$\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \mathcal{A}\left(\phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_1)\phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_2)....\phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_N)\right)$$

$$= \mathcal{A}\left(\prod_{i=1}^{N}\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}_i)\right)$$

Slater determinant

$$\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_1) & \phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_2) & \cdots & \phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_N) \\ \phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_1) & \phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_2) & \cdots & \phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_N) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_1) & \phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_2) & \cdots & \phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_N) \end{vmatrix}$$

Hartree-Fock approximation to electronic wavefunction -- continued

Variational estimate of electron energy in Hartree-Fock approximation

$$E = \frac{\left\langle \Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right| H \left|\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle}{\left\langle \Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) \middle| \Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle}$$

Let $\mathfrak{F}_{HF} \equiv \left\langle \Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right| H \left|\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle$

and require $\left\langle \phi_{n_i\mathbf{k}_i\sigma_i} \middle| \phi_{n_j\mathbf{k}_j\sigma_j}\right\rangle = \delta_{ij}$, then the variational equations for the Hartree Fock orbitals are:

$$\frac{\partial \mathfrak{F}_{HF}}{\partial \phi_{n_i\mathbf{k}_i\sigma_i}{}^*} = \sum_j \lambda_{ij}\phi_{n_j\mathbf{k}_j\sigma_j}$$

Variational equation for Hartree-Fock approximation -- continued

$$\frac{\partial \mathcal{F}_{HF}}{\partial \phi_{n_i \mathbf{k}_i \sigma_i}{}^*} = \sum_j \lambda_{ij} \phi_{n_j \mathbf{k}_j \sigma_j}$$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{Ne}(\mathbf{r}) + V_{ee}(\mathbf{r}) + V_{ex}(\mathbf{r}) \right) \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}) = \sum_j \lambda_{ij} \phi_{n_j \mathbf{k}_j \sigma_j}$$

Electron-exchange interaction:

$$V_{ex}(\mathbf{r}) \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}) \equiv -e^2 \sum_j \delta_{\sigma_i \sigma_j} \phi_{n_j \mathbf{k}_j \sigma_j}(\mathbf{r}) \int d^3 r' \frac{\phi_{n_j \mathbf{k}_j \sigma_j}{}^*(\mathbf{r}') \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Note that in the Hartree-Fock formalism, there is no spurious electron self-interaction.

9/21/2015 PHY 752 Fall 2015 -- Lecture 12 10

Hartree-Fock approximation – continued

As for the Hartree formulation, the Hartree-Fock equations must be solved iteratively. At convergence, the Hartree-Fock electronic energy can be calculated from the one-electron orbitals and the charge density

$$E_{HF} = E_K + E_{Ne} + E_{ee} + E_{ex}$$

$$E_{ex} = -\frac{e^2}{2} \sum_{i,j} \delta_{\sigma_i \sigma_j} \int d^3 r \phi_{n_i \mathbf{k}_i \sigma_i}{}^*(\mathbf{r}) \phi_{n_j \mathbf{k}_j \sigma_j}(\mathbf{r}) \int d^3 r' \frac{\phi_{n_j \mathbf{k}_j \sigma_j}{}^*(\mathbf{r}') \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

9/21/2015 PHY 752 Fall 2015 -- Lecture 12 11

Note: Hartree-Fock theory is generally the starting approximation for "quantum chemical" treatments of the electronic structure of atoms and molecules. More accurate calculations are based on multi-determinant expansions: $\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = \sum_{\mu=1}^{M} C_\mu^\alpha S_\mu(\{\mathbf{r}_i\})$

where

$$S_\mu(\{\mathbf{r}_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{n_1 \mathbf{k}_1 \sigma_1}(\mathbf{r}_1) & \phi_{n_1 \mathbf{k}_1 \sigma_1}(\mathbf{r}_2) & \cdots & \phi_{n_1 \mathbf{k}_1 \sigma_1}(\mathbf{r}_N) \\ \phi_{n_2 \mathbf{k}_2 \sigma_2}(\mathbf{r}_1) & \phi_{n_2 \mathbf{k}_2 \sigma_2}(\mathbf{r}_2) & \cdots & \phi_{n_2 \mathbf{k}_2 \sigma_2}(\mathbf{r}_N) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_{n_N \mathbf{k}_N \sigma_N}(\mathbf{r}_1) & \phi_{n_N \mathbf{k}_N \sigma_N}(\mathbf{r}_2) & \cdots & \phi_{n_N \mathbf{k}_N \sigma_N}(\mathbf{r}_N) \end{vmatrix}$$

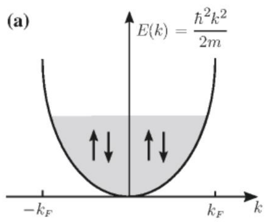
For $M \to \infty$, the calculated energy converges to the exact result E_{exact}

$E_{\text{correlation}} = E_{\text{exact}} - E_{\text{HF}}$

9/21/2015 PHY 752 Fall 2015 -- Lecture 12 12

Evaluation of the Hartree-Fock equations for the jellium model – homogeneous electron gas

$$\Psi_0 = \mathcal{A}\{W_{\mathbf{k}_1}\alpha\ W_{\mathbf{k}_1}\beta \cdots W_{\mathbf{k}_{N/2}}\alpha\ W_{\mathbf{k}_{N/2}}\beta\} \quad \text{with} \quad W(\mathbf{k}_i, \mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_i\cdot\mathbf{r}}.$$



Hartree-Fock Equations

$$\left[\frac{\mathbf{p}^2}{2m} + V_{\text{nucl}}(\mathbf{r}) + V_{\text{coul}}(\mathbf{r}) + V_{\text{exch}}\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

$$V_{\text{coul}}(\mathbf{r}) = 2\sum_j^{N/2} \langle \phi_j(\mathbf{r}')| \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\phi_j(\mathbf{r}')\rangle,$$

$$V_{\text{exch}}\phi_i(\mathbf{r}) = -\sum_j^{N/2} \langle \phi_j(\mathbf{r}')| \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\phi_i(\mathbf{r}')\rangle \phi_j(\mathbf{r}).$$

For jellium model: $V_{\text{coul}}(\mathbf{r}) = -V_{\text{nucl}}(\mathbf{r})$

$$V_{\text{exch}}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} = -\sum_{\mathbf{q}}^{(\text{occ})} \frac{1}{\sqrt{V}} e^{i\mathbf{q}\cdot\mathbf{r}} \int \frac{1}{\sqrt{V}} e^{-i\mathbf{q}\cdot\mathbf{r}'} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}'}\, d\mathbf{r}'$$

$$= -\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{q}}^{(\text{occ})} \int \frac{1}{V} e^{-i(\mathbf{k}-\mathbf{q})\cdot(\mathbf{r}-\mathbf{r}')} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}'$$

$$= -\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \frac{1}{V} \sum_{q<k_F} \frac{4\pi e^2}{|\mathbf{k}-\mathbf{q}|^2}.$$

Some details --

$$V_{\text{exch}}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} = -\sum_{\mathbf{q}}^{(\text{occ})} \frac{1}{\sqrt{V}} e^{i\mathbf{q}\cdot\mathbf{r}} \int \frac{1}{\sqrt{V}} e^{-i\mathbf{q}\cdot\mathbf{r}'} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}'}\, d\mathbf{r}'$$

$$= -\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{q}}^{(\text{occ})} \int \frac{1}{V} e^{-i(\mathbf{k}-\mathbf{q})\cdot(\mathbf{r}-\mathbf{r}')} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}'$$

$$= -\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \frac{1}{V} \sum_{q<k_F} \frac{4\pi e^2}{|\mathbf{k}-\mathbf{q}|^2}.$$

Note that: $\int e^{-i\mathbf{Q}\cdot\mathbf{r}} \frac{1}{r} d^3r = \lim_{\epsilon\to 0}\left(\int e^{-i\mathbf{Q}\cdot\mathbf{r}-\epsilon r}\frac{1}{r}d^3r\right)$

$$\int e^{-i\mathbf{Q}\cdot\mathbf{r}-\epsilon r}\frac{1}{r}d^3r = \int e^{-i\mathbf{Q}\cdot\mathbf{r}-\epsilon r}\frac{1}{r} r^2 dr\ d\cos\theta\ d\phi = -2\pi\int_0^\infty r dr e^{-\epsilon r}\int_{-1}^{1} d\cos\theta\ e^{-iQr\cos\theta}$$

$$= -2\pi\int_0^\infty r dr e^{-\epsilon r}\left(\frac{e^{-iQr}-e^{iQr}}{-iQr}\right) = \frac{4\pi}{Q^2+\epsilon^2}$$

More details

$$I(k) = \frac{1}{V}\sum_{q<k_F}\frac{4\pi e^2}{|\mathbf{k}-\mathbf{q}|^2} = \frac{4\pi e^2}{(2\pi)^3}\int_{q<k_F}\frac{1}{|\mathbf{k}-\mathbf{q}|^2}\,d\mathbf{q}.$$

$$I(k) = \frac{4\pi e^2}{(2\pi)^3}\int_{q<k_F}\frac{1}{q^2-2kq\cos\theta+k^2}\,q^2\sin\theta\,d\theta\,d\phi\,dq.$$

$$I(k) = \frac{e^2}{\pi}\frac{1}{k}\int_0^{k_F} q\ln\frac{k+q}{k-q}\,dq = \frac{e^2}{\pi}\frac{1}{k}\left[kq-\frac{1}{2}(k^2-q^2)\ln\frac{k+q}{k-q}\right]_0^{k_F}.$$

We thus obtain

$$\boxed{I(k) = \frac{2e^2k_F}{\pi}F\left(\frac{k}{k_F}\right)},$$

where the function $F(x)$ is given by

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

Eigenvalues of the plane wave orbitals:

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

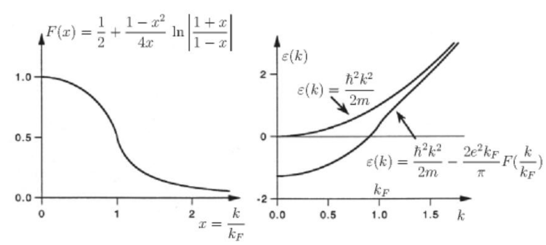


Figure 4.4 (a) Schematic plot of the function $F(x)$. (b) Kinetic energy and Hartree-Fock orbital energy as a function of the wavevector k for the homogeneous electron gas. Energies are in Rydbergs, k is in units of a_B^{-1} (inverse Bohr radius), and we have taken $k_F = 1/a_B$.

Total electronic energy of homogeneous electron gas in Hartree-Fock approximation

$$E_0^{(\mathrm{HF})} = 2\sum_{k<k_F}\frac{\hbar^2k^2}{2m} - 2\sum_{k<k_F}\frac{1}{2}\frac{2e^2k_F}{\pi}F\left(\frac{k}{k_F}\right),$$

$$E_0^{(\mathrm{HF})} = N\left[\frac{3}{5}\frac{\hbar^2k_F^2}{2m}-\frac{3}{4}\frac{e^2k_F}{\pi}\right].$$

Some details:

$$F_{\mathrm{av}} = \int_0^1 x^2F(x)\,dx\Big/\int_0^1 x^2\,dx = 3\int_0^1 x^2F(x)\,dx = \frac{3}{4}.$$

The indefinite integral

$$\int x(1-x^2)\ln\frac{1+x}{1-x}\,dx = \frac{1}{2}x-\frac{1}{6}x^3-\frac{1}{4}(1-x^2)^2\ln\frac{1+x}{1-x}$$

Some ideas –

John Slater suggested that the average exchange potential of the homogeneous electron gas could be used to estimate the exchange interaction of a material

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

$$V_{\text{jellium exchange}} = -\frac{2e^2 k_F}{\pi} F\left(\frac{k}{k_F}\right)$$

$$\left\langle V_{\text{jellium exchange}} \right\rangle = -\frac{2e^2 k_F}{\pi}\frac{3}{4}$$

For a electron gas of density n: $k_F = \left(3\pi^2 n\right)^{1/3}$

$$V_{\text{exch}}^{(\text{Slater})}(\mathbf{r}) = -\frac{3}{2}\frac{e^2}{\pi}[3\pi^2 n(\mathbf{r})]^{1/3}.$$

Kohn-Sham's approximate exchange

Total exchange energy per unit volume of jellium model

$$E_{\text{jellium exchange}} = -\frac{N}{V}\frac{3}{4}\frac{e^2\left(3\pi^2 n\right)^{1/3}}{\pi} = -\frac{3}{4}\frac{e^2\left(3\pi^2\right)^{1/3} n^{4/3}}{\pi}$$

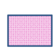
Kohn & Sham argued that the effective exchange potential should be determined from the density derivative:

$$V_{\text{jellium exchange}} = \frac{\partial E_{\text{jellium exchange}}(n)}{\partial n} = -\frac{e^2\left(3\pi^2 n\right)^{1/3}}{\pi}$$

$$V_{ex}^{KS}(\mathbf{r}) = -\frac{e^2\left(3\pi^2 n(\mathbf{r})\right)^{1/3}}{\pi} \qquad V_{ex}^{Slater}(\mathbf{r}) = -\frac{3}{2}\frac{e^2\left(3\pi^2 n(\mathbf{r})\right)^{1/3}}{\pi}$$

Comment on the spatial dependence of these approximations

For a electron gas of density n: $k_F = \left(3\pi^2 n\right)^{1/3}$



$$\Rightarrow k_F(\mathbf{r}) = \left(3\pi^2 n(\mathbf{r})\right)^{1/3}$$