Chapter 3

Density functional theory

We are interested in the properties of a solid, whose interactions are described by the
hamiltonian

\[ H^e = \sum_{i=1}^{N} -\frac{\hbar^2}{2m} \nabla_{\vec{r}_i}^2 + v(\vec{r}) + \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \sum_{i \neq j}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|}. \]

We assume that the ground state of this system is not degenerate,

\[ H^e \Phi = E^e \Phi, \]

and that the system is not magnetic, i.e., that the density of particles with spin up is the
same as the density of particles with spin down:

\[ n_↑(\vec{r}) = n_↓(\vec{r}). \]

Accordingly, the total density of particles in this system is

\[ n(\vec{r}) = n_↑(\vec{r}) + n_↓(\vec{r}) = \langle \Phi | \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) | \Phi \rangle; \]

\[ n_↑(\vec{r}) = n_↓(\vec{r}) = \frac{n(\vec{r})}{2}. \]

Though the assumption of non-degeneracy is not strictly necessary, we will use it in the
following for the sake of simplicity.

3.1 Hohenberg-Kohn theorem

The Hohenberg-Kohn theorem [P. Hohenberg, W. Kohn, Phys. Rev. 136, B864 (1964)]
asserts that ”the expectation value of \( H^e \) is a functional of the particle density \( n(\vec{r}) \).”

\[ \langle \Phi | H^e | \Phi \rangle = E_v[n] = \int v(\vec{r})n(\vec{r}) d^3\vec{r} + F[n]; \]

\[ \langle \Phi | H^e | \Phi \rangle = \langle \Phi | v | \Phi \rangle + \langle \Phi | T^e + V^{e-e} | \Phi \rangle. \]
Proof: We know that $F$

$$F = \langle \Phi | T^e + V^e - e | \Phi \rangle,$$

is a functional of $\Phi$. $\Phi$ is the ground state of any $N$-particle system. We will first show that $\Phi$ is a functional of $n(\vec{r})$ [as long as our consideration is restricted to functions $n(\vec{r}) = \langle \Phi | \sum_i \delta(\vec{r} - \vec{r}_i) | \Phi \rangle$]:

$$\Phi = \Phi[n(\vec{r})].$$

We know that the opposite statement holds, i.e., that $n(\vec{r})$ is a functional of $\Phi$:

$$n(\vec{r}) = \langle \Phi | \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) | \Phi \rangle.$$

The question is whether this relation is bijective. To prove that it is, i.e., that $\Phi = \Phi[n]$, we will use the *reductio ad absurdum* method. As an original starting point, let us consider two physically different potentials $v(\vec{r}) \neq \tilde{v}(\vec{r})$, i.e., such that satisfy

$$v(\vec{r}) - \tilde{v}(\vec{r}) \neq \text{constant.} \quad (3.1)$$

These two potentials define two Hamiltonian operators $H^e$ and $\tilde{H}^e$ [Reminder: For simplicity, here we consider the operator $H$ with a non-degenerate ground state (GS), but the proof can be generalized to systems with degenerate GS’s; see M. Levy, *Proc. Natl. Acad. Sci. USA* 76, 6062 (1979)].

**Assumption 1:** Both Hamiltonian operators have the same ground state wavefunction. Then,

$$(\tilde{H}^e - H^e)\Phi_0 = \sum_{i=1}^N \{\tilde{v}(\vec{r}_i) - v(\vec{r}_i)\} \Phi_0 = (\tilde{E}_0^e - E_0^e)\Phi_0$$

$$= \{\tilde{v}(\vec{r}) - v(\vec{r})\} \Phi_0$$
and
\[ \sum_{i=1}^{N} \{ \tilde{v}(\vec{r}_i) - v(\vec{r}_i) \} = \tilde{E}_0^e - E_0^e. \]  
(3.2)

Expression (3.2) means that \( \tilde{v}(\vec{r}) - v(\vec{r}) \) is a constant (with an exception of a discrete set of points where \( \Phi_0 = 0 \)), which contradicts our starting point [Eq. (3.1)]. Thus, the assumption that \( H^e \) and \( \tilde{H}^e \) have the same ground state wavefunction is wrong. Therefore,

\[ \Phi_0 \neq \tilde{\Phi}_0. \]

**Assumption 2:** Even if \( \Phi_0 \) and \( \tilde{\Phi}_0 \) are different, they define the same particle density \( n(\vec{r}) \):

\[ n(\vec{r}) = \langle \Phi_0 | \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) | \Phi_0 \rangle = \langle \tilde{\Phi}_0 | \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) | \tilde{\Phi}_0 \rangle. \]

Then,

\[ E_0^e = \langle \Phi_0 | H^e | \Phi_0 \rangle < \langle \tilde{\Phi}_0 | \tilde{H}^e | \tilde{\Phi}_0 \rangle \]
\[ = \langle \tilde{\Phi}_0 | \tilde{H}^e - \sum_{i=1}^{N} \tilde{v}(\vec{r}_i) + \sum_{i=1}^{N} v(\vec{r}_i) | \tilde{\Phi}_0 \rangle; \]

\[ E_0^e < \tilde{E}_0^e + \langle \tilde{\Phi}_0 | \tilde{H}^e - \sum_{i=1}^{N} \{ v(\vec{r}_i) - \tilde{v}(\vec{r}_i) \} | \tilde{\Phi}_0 \rangle; \]

\[ E_0^e < \tilde{E}_0^e + \int \{ v(\vec{r}) - \tilde{v}(\vec{r}) \} n(\vec{r}) \, d^3\vec{r}. \]  
(3.3)

Analogously,

\[ \tilde{E}_0^e = \langle \tilde{\Phi}_0 | \tilde{H}^e | \tilde{\Phi}_0 \rangle < \langle \Phi_0 | H^e | \Phi_0 \rangle \]
\[ = \langle \Phi_0 | H^e - \sum_{i=1}^{N} v(\vec{r}_i) + \sum_{i=1}^{N} \tilde{v}(\vec{r}_i) | \Phi_0 \rangle; \]

\[ \tilde{E}_0^e < E_0^e - \int \{ v(\vec{r}) - \tilde{v}(\vec{r}) \} n(\vec{r}) \, d^3\vec{r}. \]  
(3.4)

Adding (3.3) and (3.4), we get

\[ E_0^e + \tilde{E}_0^e < E_0^e + \tilde{E}_0^e, \]

which contradicts itself. Therefore, Assumption 2 is wrong and we have proven that
two different groundstates $\Phi_0$ and $\tilde{\Phi}_0$ define two different densities of particles $n(\vec{r})$ and $\tilde{n}(\vec{r})$.

The proof allows us to state the following.

a) $E_v[n] = \langle \Phi | H^e | \Phi \rangle$ is a functional of $\bar{n}(\vec{r})$ since $E[n]$ is a uniquely defined functional of $\Phi$ and, as we have seen, $\Phi$ is a uniquely defined functional of $n$.

b) In the expression

$$E_v[n] = \int n(\vec{r}) v(\vec{r}) \, d^3\vec{r} + F[n],$$

$F[n]$ is a universal functional of $n(\vec{r})$, i.e., it is independent of the “external potential” $v(\vec{r})$.

c. $E_{v0}[n]$ is minimal at the correct particle density with condition $\int n(\vec{r}) \, d^3\vec{r} = N$. This minimum defines the ground state energy and the particle density of the ground state:

$$E^e_0 = \text{Min}_{n(\vec{r})} E_{v0}[n].$$

By virtue of the Rayleigh-Ritz principle, $E_{v0}[n]$ has the obvious property:

$$E_0 < E_{v0}[n] \text{ for } n \neq n_0;$$
$$E_0 = E_{v0}[n_0].$$

Therefore, the exact ground state density can be determined by minimization of the functional $E_{v0}[n]$:  

$$E_0 = \text{Min}_{n \in \mathbb{N}} E_{v0}[n].$$

The variation principle for $\langle \Phi | H^e | \Phi \rangle$ is exactly mapped onto the variation principle for $E_v[n]$:  

$$\delta \left\{ E_v[n] - \mu \left( \int n(\vec{r}) \, d^3\vec{r} - N \right) \right\} = 0,$$

with the condition that the total number of particles has to be conserved and equal to $N$ (Lagrange multipliers). The other two conditions that we also have to take into account are

$$n(\vec{r}) \geq 0$$

and that $n(\vec{r})$ has to be continuous.

The advantage of the density functional (DF) formulation of a many-body problem with respect to the Hartree-Fock (HF) theory (Fig.3.1):

HF $\rightarrow$ Wavefunctions with $10^{23}$ coordinates are introduced into the functional to be minimized. Since such a functional is impossible to minimize in practice, we made approximations before applying minimization (by choosing an ansatz for $\Phi$).

DF $\rightarrow$ Here, we have functions with three coordinates to be introduced into the functional, and up to now the DF formulation has been exact.
3.1.1 Extensions of the Hohenberg-Kohn theorem

i. Mathematical extensions.

- Degenerate ground states.

- \( v \)-representability: A function \( n(\vec{r}) \) is termed pure-state \( v \)-representable if it is the density of a (possibly degenerate) ground state of a Hamiltonian with some suitably chosen local external potential \( v(\vec{r}) \) (with the number of particles \( N \) and their mutual interaction \( w(\vec{r}, \vec{r}') \) being specified).

- Dependence of the considered functionals on the particle number \( N \). This issue is important when dealing with the variational formulation,

\[
\frac{\delta}{\delta n} \left( E_v[n] - \mu \int n(\vec{r}) \, d^3\vec{r} \right) = 0,
\]

where the condition of a particular number of particles is specified via the Lagrange multiplier \( \mu \). This formulation leads to the Euler equation:

\[
\frac{\delta E_v[n]}{\delta n(\vec{r})} = \mu. \tag{3.5}
\]

If now one lets \( n_N(\vec{r}) \) be the solution of (3.5) with particle number \( N \) and \( E_N \) is the corresponding ground state energy,

\[
E_N = E_v[n_N],
\]

then, for each solution \( n_N(\vec{r}) \), the equation (3.5) is satisfied with a certain number \( \mu = \mu(N) \), and

\[
\mu(N) = \frac{\partial E_N}{\partial N},
\]
is the chemical potential of the system. If $\mu(N)$ is assumed to be a continuous function of $N$, a paradox arises in the formalism. This paradox has been extensively discussed in J. P. Perdew and M. Levy, Phys. Rev. B 31, 6264 (1985).

ii. Extensions based on the physical variety of systems.

- Spin-polarized systems.

An external magnetic field applied to an electronic system couples to both the electronic orbital current and the particle spin. In the presence of the magnetic field, the original hamiltonian

$$\hat{H} = \hat{T} + \hat{W},$$

with $\hat{T}$ being the kinetic term and $\hat{W}$ the Coulomb term, is extended to

$$\hat{H} = \hat{T} + \hat{W} + \hat{U},$$

where $\hat{U}$ contains the single particle contribution:

$$\hat{U} = \int d^3\vec{r} \left[ v(\vec{r})\hat{n}(\vec{r}) - \vec{B}(\vec{r})\hat{m}(\vec{r}) \right].$$

The particle density is in this case defined as

$$\hat{n}(\vec{r}) = \sum_\alpha \hat{\Psi}_\alpha(\vec{r})\hat{\Psi}_\alpha(\vec{r}) = \hat{n}_\uparrow(\vec{r}) + \hat{n}_\downarrow(\vec{r}),$$

where $\hat{\Psi}_\alpha(\vec{r})$ and $\hat{\Psi}_\alpha(\vec{r})$ are field operators: $\hat{\Psi}_\alpha(\vec{r})$ creates a particle with spin $\alpha$ at position $\vec{r}$, whereas $\hat{\Psi}_\alpha(\vec{r})$ annihilates a particle with spin $\alpha$ at position $\vec{r}$. The magnetic moment density is defined as

$$\hat{m}(\vec{r}) = -\mu_B \sum_{\alpha\beta} \hat{\Psi}_\alpha(\vec{r}) \vec{\sigma}_{\alpha\beta} \hat{\Psi}_\beta(\vec{r}),$$

where $\mu_B = \frac{e\hbar}{2mc}$ is the Bohr magneton and $\vec{\sigma}_{\alpha\beta}$ are the Pauli matrices. In particular,

$$\hat{m}_z(\vec{r}) = -\mu_B (\hat{n}_\uparrow(\vec{r}) - \hat{n}_\downarrow(\vec{r})).$$

With these definitions, one may write the single-particle operator $\hat{U}$ as

$$\hat{U} = \sum_{\alpha\beta} \int d^3\vec{r} \vec{\Psi}_\alpha(\vec{r})u_{\alpha\beta}(\vec{r})\vec{\Psi}_\beta(\vec{r}),$$

where

$$u_{\alpha\beta}(\vec{r}) = v(\vec{r})\delta_{\alpha\beta} - \mu_B \vec{B}(\vec{r})\vec{\sigma}_{\alpha\beta}. $$
Depending on the choice of $\hat{U}$, one either deals with the ground state density and the ground state magnetization:

$$n(\vec{r}) = \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle,$$

$$\vec{m}(\vec{r}) = \langle \Psi | \hat{m}(\vec{r}) | \Psi \rangle,$$

or with the ground state spin density matrix:

$$n_{\alpha\beta}(\vec{r}) = \langle \Psi | \hat{\Psi}^\dagger_\alpha(\vec{r}) \hat{\Psi}_\beta(\vec{r}) | \Psi \rangle.$$

In either case, one deals with four independent real functions!

The DFT approach can be extended to define an explicit spin dependent functional: two different non-degenerate ground states $|\Psi\rangle \neq |\Psi'\rangle$ are always characterized by different spin density matrices $n_{\alpha\beta}(\vec{r}) \neq n'_{\alpha\beta}(\vec{r})$ or, equivalently, $[n(\vec{r}), \vec{m}(\vec{r})] \neq [n'(\vec{r}), \vec{m}'(\vec{r})]$. Furthermore, in the limit $B \rightarrow 0$, the spin-dependent density functional formalism leads to a density functional description of a system having a spin-polarized ground state without any external magnetic field.

- Finite temperature ensembles.

Up to now, we have restricted ourselves to the ground state properties of a system, i.e., to a $T = 0$ (temperature) case. In order to establish an equation of state, one requires for the DFT formalism an extension to finite temperatures, which is represented by the thermodynamic density functional theory.

In a grand canonical ensemble at a given temperature $T$ and chemical potential $\mu$, the grand canonical potential is given by

$$\Omega = E - \mu N - TS,$$

$E$: internal energy,
$N$: particle number,
$S$: entropy.

The grand canonical potential $\Omega$ is minimal in an equilibrium state. The microscopic calculation of equilibrium properties involves the grand canonical statistical operator:

$$\hat{\rho} = \exp \left[ -\beta (\hat{H} - \mu \hat{N}) \right] / \text{Tr} \left\{ \exp \left[ -\beta (\hat{H} - \mu \hat{N}) \right] \right\},$$

with

$$\beta = \frac{1}{k_B T},$$

$$\hat{N} = \sum_\alpha \int d^3 \vec{r} \hat{\Psi}^\dagger_\alpha(\vec{r}) \hat{\Psi}_\alpha(\vec{r}).$$
In terms of $\hat{\rho}$, the grand canonical potential and the equilibrium density are written as, respectively,

$$\Omega = \text{Tr} \left\{ \hat{\rho}(\hat{H} - \mu \hat{N} + \frac{1}{\beta} \ln \hat{\rho}) \right\}$$

and

$$n(\vec{r}) = \text{Tr} \left\{ \hat{\rho} \left( \sum_{\alpha} \hat{\Psi}_{\alpha}^\dagger(\vec{r}) \hat{\Psi}_{\alpha}(\vec{r}) \right) \right\}.$$  

Analogously to the $T = 0$ case, it can be proven that $\hat{\rho}$ is a functional of the equilibrium density, $\hat{\rho} = \hat{\rho}[n]$, and that the density functional for the grand canonical potential is universal:

$$\Omega_{\nu - \mu}[n] = \int d^3\vec{r} (v(\vec{r}) - \mu)n(\vec{r}) + F[n],$$

$$F[n] = \text{Tr} \left\{ \hat{\rho}[n] \left( \hat{T} + \hat{W} + \frac{1}{\beta} \ln \hat{\rho}[n] \right) \right\}.$$

– Bose systems.

One would need the bosonic DFT, when considering, for instance, the inhomogeneous He$_4$ system. But, is a density functional description of many-boson systems possible at all? Since the question of statistics does not enter into the arguments of Hohenberg and Kohn, their theorem holds for both the bosonic and fermionic cases. The two cases will be distinguished by the explicit form of the density functionals involved. In the case of bosonic systems, one searches for symmetric $N$-particle wavefunctions given a specified density.

### 3.2 Kohn-Sham scheme


The variational principle of Hohenberg and Kohn allows the determination of the exact ground state density of a specified many-particle system but the explicit form of $F[n]$ is not known.

$$\langle \Psi | H^e | \Psi \rangle = E_v[n] = \int v(\vec{r}) n(\vec{r}) d^3\vec{r} + F[n], \quad (3.6)$$

with

$$F[n] = \langle \Psi | T^e + V^{e-e} | \Psi \rangle \quad (3.7)$$

Kohn and Sham proposed the following scheme. Since the ground state of the interacting system is uniquely defined by the ground state density $n$, Kohn and Sham introduce a fictitious non-interacting system that generates the same density as the interacting
system. Therefore by solving the set of equations for the non-interacting system it is possible to obtain the exact density of the interacting system.

The energy functional (3.6) can be rewritten as

$$E_v[n] = T_s[n] + \int v(\vec{r}) n(\vec{r}) \, d^3\vec{r} + E_{\text{Hartree}}[n] + E_{\text{xc}}[n],$$

where

- $E_{\text{Hartree}}[n] = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \int \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d^3\vec{r} \, d^3\vec{r}'$,
- $T_s[n]$ is the functional of the kinetic energy of non-interacting electrons and
- $E_{\text{xc}}[n]$ is the exchange-correlation potential given by

$$E_{\text{xc}}[n] = \left\{ \langle \Phi | H^e | \Phi \rangle - \int v(\vec{r}) n(\vec{r}) \, d^3\vec{r} \right\} - T_s[n] - E_{\text{Hartree}}[n]$$

$$= F[n] - T_s[n] - E_{\text{Hartree}}[n].$$

$E_{\text{xc}}$ is called the exchange-correlation potential because it contains information about exchange and correlation and also the difference between the exact and the non-interacting kinetic energy. We do not know its formal expression. Earlier we saw that the variation principle leads to the equation

$$\delta \left\{ E_v[n] - \mu \left( \int n(\vec{r}) \, d^3\vec{r} - N \right) \right\} = 0;$$

$$\frac{\delta E_v[n]}{\delta n(\vec{r})} = \mu.$$

With the above introduced partition of $F[n]$, this equation becomes

$$\frac{\delta T_s[n]}{\delta n(\vec{r})} + v_{\text{eff}}(\vec{r}) = \mu,$$

(3.8)

with

$$v_{\text{eff}}(\vec{r}) = \frac{\delta \left\{ \int v(\vec{r}) n(\vec{r}) \, d^3\vec{r} + E_{\text{Hartree}}[n] + E_{\text{xc}}[n] \right\}}{\delta n(\vec{r})}$$

$$= v(\vec{r}) + \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d^3\vec{r}' + \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{r})}.$$

Equation (3.8) is formally an equation of non-interacting particles moving in the potential $v_{\text{eff}}(\vec{r})$ since $T_s[n]$ corresponds to the kinetic energy of non-interacting particles of density $n(\vec{r})$. This sounds as a good news as up to now we have not made any approximations
but yet achieved a great simplification of the problem. It is not clear, however, whether the functional $T_s[n]$ exists for all $n$ of $E_v[n]$.

Kohn and Sham adopted the orbital picture. They assumed that

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_{\theta_i}(\mathbf{r})|^2,$$

where $\varphi_{\theta_i}(\mathbf{r})$ are single-particle wavefunctions. It is plausible that a set of densities defined as (3.9) cover all physically meaningful densities. Substituting

$$T_s[n] = T_s[\{\varphi^*_{\theta_k}(\mathbf{r}), \varphi_{\theta_k}(\mathbf{r})\}] = \sum_{i=1}^{N} \langle \varphi_{\theta_i}(\mathbf{r}) | - \frac{\hbar^2}{2m} \nabla^2 | \varphi_{\theta_i}(\mathbf{r}) \rangle$$

into (3.8), we get

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(\mathbf{r}) \right\} \varphi_{\theta_i}(\mathbf{r}) = \epsilon_{\theta_i} \varphi_{\theta_i}(\mathbf{r}).$$

This equation together with

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_{\theta_i}(\mathbf{r})|^2$$

and

$$v^{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d^3\mathbf{r}' + \frac{\delta E^{xc}[n]}{\delta n(\mathbf{r})}$$

constitute the Kohn-Sham equations. These equations have to be solved self-consistently. The Kohn-Sham wavefunction is a single Slater determinant constructed from a set of orbitals that are the lowest energy solutions of the previous equations.

Even though we do not know the explicit functional dependence of $T_s$ on $n$, through the introduction of $n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_{\theta_i}(\mathbf{r})|^2$, it can be exactly considered [see (3.10)]. The disadvantage of this procedure is that we are going back to considering $N$ one-particle wavefunctions, which is exactly what we wanted to avoid!

Let us show that $T_s$ is a functional of $n$. Indeed, in the expression

$$T_s[n] = \sum_{i=1}^{N} \langle \varphi_{\theta_i}(\mathbf{r}) | - \frac{\hbar^2}{2m} \nabla^2 | \varphi_{\theta_i}(\mathbf{r}) \rangle$$

$$= \sum_{i=1}^{N} \epsilon_{\theta_i} - \int v^{\text{eff}}(\mathbf{r}) n(\mathbf{r}) \, d^3\mathbf{r},$$

$v^{\text{eff}}(\mathbf{r})$ has to be calculated from equation (3.11) and $\epsilon_{\theta_i}$ is obtained from the Kohn-Sham equations. In fact, formally,

$$\tilde{T}[n] = \sum_{i=1}^{N} \epsilon_{\theta_i} - \int v^{\text{eff}}[n](\mathbf{r}) n(\mathbf{r}) \, d^3\mathbf{r},$$
since $v^{\text{eff}}$ is a functional of $n$, or

$$T_s[n] = \int t_s[n](\vec{r}) \, d^3\vec{r},$$

where $t_s[n]$ is the mean kinetic energy per particle of a system of non-interacting electrons with density $n(\vec{r})$.

Until now, we have not made any approximations. Note that, contrary to the Hartree and Hartree-Fock approaches where we chose an expression for the ground state wavefunction, this time we first applied the variational principle for the ground state, and only afterwards we shall introduce approximations.

By experience, it is also known that it is important that $T_s[n]$ is exactly considered. The Kohn-Sham ansatz allows to treat $T_s[n]$ exactly, which was not the case within the Thomas-Fermi approach.

### 3.2.1 Jellium Model

Let us consider the Jellium model, where $T_s[n]$ can be written explicitly:

$$T_s[n] = \sum_{i=1}^{N} \langle \varphi_{\theta_i} | - \frac{\hbar^2}{2m} \nabla^2 | \varphi_{\theta_i} \rangle$$

$$= \frac{1}{V_g} \frac{V_g}{(2\pi)^3} \frac{2}{2m} \frac{\hbar^2}{2m} \int_{0}^{k_F} k^2 d^3k$$

$$= \frac{1}{V_g} \frac{4\pi^2}{(2\pi)^3} \frac{2}{2m} \frac{\hbar^2}{2m} \int_{0}^{k_F} k^4 dk = \frac{V_g \hbar^2}{5\pi^2} \frac{k_F^5}{2m}$$

$$= \frac{1}{V_g} \frac{V_g}{5\pi^2} \frac{\hbar^2}{2m} (3\pi^2 n)^{5/3} = T_{s\text{Jellium}}[n].$$

where the one-particle orbitals were taken as plane waves.

In the case of the Jellium model, the $\frac{\delta T_s[n]}{\delta n(\vec{r})}$ term in the Kohn-Sham equations is

$$\frac{\delta T_s[n]}{\delta n(\vec{r})} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = \frac{\hbar^2}{2m} k_F^2.$$

We have obtained the kinetic energy of the Jellium system as a functional of $n$ explicitly. Note that

$$\frac{\delta T_s}{\delta n} = \frac{\hbar^2}{2m} k_F^2$$

provides the maximal kinetic energy, i.e., the energy of the particles at the Fermi level, and is therefore bigger than the mean kinetic energy. In general, we will be using either
The second functional that we do not know explicitly is
\[ v^{xc}(\mathbf{r}) = \frac{\delta E^{xc}[n]}{\delta n(\mathbf{r})}. \]

Analogously to \( T_s \), \( \frac{\delta E^{xc}[n]}{\delta n(\mathbf{r})} \) provides the value of the exchange-correlation interaction at the Fermi level. \( E^{xc}[n] \) is a universal functional, i.e., it is independent of the system. Unfortunately, we do not know the exact form of \( E^{xc}[n] \). It is also not clear whether it is at all possible to write this functional in a closed way or whether \( E^{xc} \) behaves similar to \( T_s \).

By again considering the Jellium model (\( v(\mathbf{r}) = \text{constant} \)), we can expand \( E^{xc}[n] \) in powers of \( \nabla n \):
\[ E^{xc}[n] = E^{xc-LDA}[n] + \mathcal{O}(\nabla n), \]
with
\[ E^{xc}[n] = \int \epsilon^{xc}[n] n(\mathbf{r}) \, d^3 \mathbf{r} \]
and
\[ E^{xc-LDA}[n] = \int \epsilon^{xc-LDA}[n] n(\mathbf{r}) \, d^3 \mathbf{r}. \]

Remember: The homogeneous electron gas, uniform electron gas or jellium model is an imaginary solid, where all the nuclear charge is homogeneously smeared over space. This material is completely isotropic and identical on every length scale. Therefore, its electron density is constant and given by
\[ n(\mathbf{r}) = n = \frac{N}{V}. \]

\( n \) is the only quantity we need in order to specify a particular homogeneous electron gas.

If electrons in a system do not interact, the energy of such a free electron gas can be easily obtained. If we have an interacting electron gas, the total energy can be calculated numerically by the quantum Monte Carlo method. By subtracting the non-interacting kinetic energy and the Hartree energy, we get a numerical result for the exchange-correlation energy \( \epsilon^{xc} \). Repeating these calculations for several densities \( n \), we can obtain the function \( \epsilon^{xc}(n) \) (not a functional!). The above introduced quantity \( \epsilon^{xc-LDA}(n) \) is defined as the exchange-correlation energy per particle in the Jellium model with a constant density \( n \). \( \epsilon^{xc-LDA}(n) \) is a function of the local density \( n \).
3.3 Local density approximation

For systems, where the particle density varies slowly, one can approximate $E^{xc}[n]$ through

$$E^{xc-\text{LDA}}[n] = \int \epsilon^{xc-\text{LDA}}(n(\vec{r})) n(\vec{r}) \, d^3\vec{r}.$$ 

This approximation has the following meaning. The exchange-correlation energy due to a particular density $n(\vec{r})$ is found by dividing the material into infinitesimally small volumes with a constant density and then assuming that each volume contributes to the total exchange-correlation energy an amount equal to the exchange-correlation energy of an individual volume filled with a homogeneous electron gas having the same overall density in this volume as the original material.

![Figure 3.2: Exchange-correlation energy per site for Jellium system of density $n$.](image)

Nowadays, the function $\epsilon^{xc-\text{LDA}}(n)$ is numerically well known. Quite frequently $\epsilon^{xc-\text{LDA}}(n)$ is also given as a function of $r_s$,

$$r_s = \sqrt[3]{\frac{3}{4\pi n}}.$$
One can calculate the exchange-correlation potential of the Kohn-Sham equations with the LDA expression for $E^{xc}[n]$ as

$$v^{xc-LDA}(\vec{r}) = \frac{\delta E^{xc-LDA}[n]}{\delta n(\vec{r})} = \frac{\partial}{\partial n} (n^{xc-LDA}(n)) \big|_{n=n(\vec{r})}.$$

Let us compare $v^{xc-LDA}$ with the Hartree-Fock-Slater (HFS) potential. Remember that the HFS potential $v^x$ was obtained by considering the exchange potential for the Jellium model in the Hartree-Fock approximation parameterized by a parameter $\alpha$. For $\alpha = 2/3$,

$$v^x = -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{\sqrt{3\pi^2 n}}.$$

In Fig. 3.3, $v^x$ is plotted together with the numerically obtained $v^{xc-LDA}$,

$$v^{xc-LDA}(r_s) = \frac{\delta E^{xc-LDA}[n]}{\delta n(\vec{r})} = \beta(r_s)v^x(r_s).$$

$\beta(r_s)$ varies between 1 and 1.3. The difference between $v^x$ and $v^{xc-LDA}$ is the correlation potential. The consideration of correlations lowers the energy with respect to only considering exchange.

### 3.4 Interpretation of the exchange-correlation potential in the DFT-LDA

$$v^{Hartree}(\vec{r}) + v^{xc}(\vec{r}) = \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\vec{r'}) - n^{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r'}.$$
- Within the **LDA** scheme, a particle at position $\vec{r}$ does not interact with particles that are distributed like $n(\vec{r})$ but it sees instead a particle distribution $n(\vec{r'}) - n_{\text{xc}}(\vec{r}, \vec{r'})$.

- The **Hartree** theory does not contain any correlation, i.e., a Hartree particle sees a distribution of other particles, which is independent of its own position.

- The **Hartree-Fock** theory contains the correlation of electrons with equal spin, which is a consequence of the Pauli principle (exchange interaction).

The Density Functional Theory is in principle exact and for the Jellium system can be exactly solved numerically. It contains both *exchange* and *correlation* originating from the Coulomb repulsion. But since the functional $\epsilon_{\text{xc}}[n]$ in its most general form is not known, the DFT in the local density approximation is only strictly valid for interacting electron systems with *slowly varying* densities.

Nevertheless, the LDA provides very good results (though not always) even for strongly inhomogeneous systems. The reason for that can be suspected to rely upon compensating errors. The LDA can be understood as an approximation for the form of the exchange-correlation hole.

*Remember:*

- The Hartree theory is not exact for any interacting many-body system;

- The Hartree-Fock theory is only exact for systems where the ground state is given by *one* Slater determinant.
### 3.5 Non-local density schemes

*Improvement of the LDA:* The exchange-correlation contribution of every infinitesimal volume is considered to be dependent not only on the local density in that volume, but also on the gradient of the density:

\[
e_{\text{xc-GGA}}(n, \nabla n) \rightarrow \text{Generalized Gradient Approximation}
\]

While there is a unique definition of \(e_{\text{xc}}\) for the LDA functional, there is some freedom in how to incorporate the density gradient and therefore there exist several versions of the generalized gradient approximation (GGA). Some of them have free parameters that are determined by fitting to a large set of experimental data. In this case, such a GGA calculation is strictly speaking not *ab-initio* anymore. There are also parameter-free GGA versions.

### 3.6 Local spin density approximation

In the formally exact DFT, one makes approximations only at the level of the *exchange-correlation energy functional* \(E_{\text{xc}}[n_\uparrow, n_\downarrow]\), which contains all *many-body effects*. The common approximations are the LDA or the local spin density approximation (LSDA),

\[
E_{\text{xc-LSDA}}[n_\uparrow, n_\downarrow] = \int e_{\text{xc-Jellium}}(n_\uparrow, n_\downarrow)n(\vec{r}) \, d^3\vec{r},
\]

which is even successful for strongly inhomogeneous systems.

*Remember:* In the Kohn-Sham scheme for the particle density,

\[
n(\vec{r}) = \sum_{i=1}^{N} \varphi^*_\theta_i(\vec{r}) \varphi_{\theta_i}(\vec{r}),
\]

where the single-particle wavefunctions \(\varphi_{\theta_i}(\vec{r})\) are the \(N\) lowest energy solutions of the Kohn-Sham equations,

\[
\hat{H}_{\text{KS}} \varphi_{\theta_i}(\vec{r}) = \epsilon_i \varphi_{\theta_i}(\vec{r}),
\]

\[
\hat{H}_{\text{KS}} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d^3\vec{r}' + V_{\text{xc}} + V_{\text{ext}},
\]

\(\varphi_{\theta_i}(\vec{r})\) are *not* the wavefunctions of electrons as they were for the Slater determinants of the HF approximation. Here, they describe *mathematical quasi-particles*, without having a direct physical meaning. Only the overall density of these quasi-particles is guaranteed to be equal to the true electron density. Therefore, the energies \(\epsilon_i\) of single quasi-particles are not single-electron energies.