1 Density Functional Theory (DFT)

1.1 The Original Idea – Thomas Fermi Theory

1.2 The Homogeneous Electron Gas

\[ \varphi_{\kappa \sigma}(r) = \frac{1}{(2\pi)^{3/2}} \exp(ik \cdot r) \chi_{\sigma} \]

(1)

Although the wavefunctions of the electrons have a spatial dependency on \( r \) the single particle density \( \rho_{\kappa \sigma} \) is constant and reads

\[ \rho_{\kappa \sigma} = \rho_{\kappa \sigma}(r) = \left| \varphi_{\kappa \sigma}(r) \right|^2 = \left| \frac{1}{(2\pi)^{3/2}} \exp(ik \cdot r) \chi_{\sigma} \right|^2 = \frac{1}{8\pi^3} \exp(-ik \cdot r) \exp(ik \cdot r) \chi_{\sigma}^\dagger \chi_{\sigma} = \frac{1}{8\pi^3}. \]

(2)

Independent of it’s quantum numbers (wavevector \( k \) and spin \( \sigma = \alpha, \beta \)) each orbital contributes equally to the total density. In case of a discrete set of single particle states \( \{ \varphi_{\kappa \sigma}(r) \}_{i=1,2,...,\infty} \) the total density is obtained by summation over all occupied states. The energy of the highest occupied single particle state is called the fermi energy \( \epsilon_F \). This has to be generalized in case of continuous

\[ \rho(r) = \sum_{\sigma=\alpha,\beta} \sum_{i=1}^{N_\sigma} \left| \varphi_{i \sigma}(r) \right|^2 \]

(3)

1.3 Thomas-Fermi Kinetic Energy Revisited

The cumbersome derivation of the Thomas-Fermi kinetic energy functional becomes much simpler in the framework of plane waves:

The kinetic energy of a basis state with wavevector \( k \) (and arbitrary spin \( \sigma = \alpha, \beta \)) is given by the expectation value

\[ t_{k,\sigma} = \int d^3r \varphi_{k \sigma}^\dagger(r) \left[ -\frac{\Delta}{2} \right] \varphi_{k \sigma}(r) = -\frac{1}{2} \frac{1}{8\pi^3} \int d^3r \exp(-ik \cdot r) \frac{1}{\Delta} \exp(ik \cdot r) \chi_{\sigma}^\dagger \chi_{\sigma} \]

(4)

\[ = -\frac{1}{16\pi^3} \int d^3r \exp(-ik \cdot r) \left[ -\frac{1}{\Delta} \right] \varphi_{k \sigma}^\dagger \varphi_{k \sigma} \]

(5)

\[ T = \sum_{\sigma=\alpha,\beta} \int_{|k|<k_F} d^3k \ t_{k,\sigma} = 2 \int_{|k|<k_F} d^3k \ t_{k,\sigma} = \frac{V}{8\pi^3} \int_{|k|<k_F} d^3k \ |k|^2 = \frac{V}{8\pi^3} 4\pi \int_0^{k_F} k^2 dk \ |k|^2 = \frac{V}{2\pi^2} \int_0^{k_F} dk \ k^4 \]

(6)

\[ \frac{V}{2\pi^2} \frac{k_F^5}{5} = \frac{V}{10\pi^2} \frac{k_F^5}{5} \]

(7)

Inserting the previously derived relation between the Fermi momentum \( k_F \) and the total density yields the kinetic energy functional

\[ T[\rho] = \frac{V k_F^5}{10\pi^2} = \frac{V}{10\pi^2} (3\pi^2 \rho)^{5/3} = \frac{3V}{10} (3\pi^2)^{2/3} \rho^{5/3} \]

(8)

1.4 Exchange in Local Density Approximation (LDA)

\[ E_x = -\frac{1}{2} \sum_{\sigma=\alpha,\beta} \sum_{\sigma'=\alpha,\beta} \int d^3k \int_{|k'|<k_F} d^3k' \ \int d^3r \int d^3r' \ \varphi_{\kappa \sigma}(r) \varphi_{\kappa \sigma'}(r') \varphi_{\kappa \sigma'}(r) \varphi_{\kappa \sigma}(r') \]

\[ \chi_{\sigma}^\dagger \chi_{\sigma'}^\dagger \chi_{\sigma'} \chi_{\sigma} \frac{1}{|r-r'|} \]

(9)

Inserting the explicit representation of the single particle states yields

\[ E_x = -\frac{1}{2} \frac{1}{64\pi^6} \sum_{\sigma=\alpha,\beta} \sum_{\sigma'=\alpha,\beta} \int d^3k \int_{|k'|<k_F} d^3k' \ \int d^3r \int d^3r' \ \exp(-ik \cdot r) \exp(-ik' \cdot r') \exp(ik \cdot r') \exp(ik' \cdot r) \chi_{\sigma}^\dagger \chi_{\sigma'}^\dagger \chi_{\sigma'} \chi_{\sigma} \]

\[ \frac{1}{|r-r'|} \]

(10)

\[ = -\frac{1}{128\pi^6} \int d^3k \int_{|k'|<k_F} d^3k' \ \int d^3r \int d^3r' \ \exp(-i(k-k') \cdot (r-r')) \chi_{\sigma}^\dagger \chi_{\sigma'}^\dagger \chi_{\sigma'} \chi_{\sigma} \frac{1}{|r-r'|} \]

\[ \sum_{\sigma=\alpha,\beta} \sum_{\sigma'=\alpha,\beta} \chi_{\sigma}^\dagger \chi_{\sigma'} \]

\[ \delta_{\sigma \sigma'} \chi_{\sigma}^\dagger \chi_{\sigma'} \]

(11)

The double summation over the scalar products of the spin functions results in a factor of 2

\[ \sum_{\sigma=\alpha,\beta} \sum_{\sigma'=\alpha,\beta} \chi_{\sigma}^\dagger \chi_{\sigma'}^\dagger \chi_{\sigma} \chi_{\sigma'} = \sum_{\sigma=\alpha,\beta} \delta_{\sigma \sigma'} = \sum_{\sigma=\alpha,\beta} 1 = 2 \]

(12)
and the integration over \( r \) and \( r' \) can be transformed to center of mass (\( \mathbf{R} = \frac{1}{2} (\mathbf{r} + \mathbf{r'}) \)) and relative coordinate (\( \mathbf{s} = \mathbf{r} - \mathbf{r'} \))

\[
E_x = -\frac{1}{64\pi^6} \int |k|<k_F \int |k'|<k_F \int d^3\mathbf{R} \int d^3\mathbf{s} \frac{\exp(-i(\mathbf{k} - \mathbf{k'}) \cdot \mathbf{s})}{|s|} \tag{13}
\]

For a moment we will forget about possible problems with the integral \( \int d^3\mathbf{R} \) as it is simply the volume of the considered space (which is actually infinite). Collecting its contributions in the prefactor \( V \) yields

\[
E_x = -\frac{V}{64\pi^6} \int |k|<k_F \int |k'|<k_F \int d^3\mathbf{s} \frac{\exp(-i\mathbf{k} \cdot \mathbf{s}) \exp(i\mathbf{k'} \cdot \mathbf{s})}{|s|} \tag{14}
\]

The complicated triple integral can be further simplified by resorting the integration order and using the independence of the two \( k \) integrations:

\[
E_x = -\frac{V}{64\pi^6} \int d^3\mathbf{s} \frac{1}{|s|} \int |k|<k_F \int |k'|<k_F \exp(-i\mathbf{k} \cdot \mathbf{s}) \exp(i\mathbf{k'} \cdot \mathbf{s}) \tag{15}
\]

\[
= -\frac{V}{64\pi^6} \int d^3\mathbf{s} \frac{1}{|s|} \int |k|<k_F \exp(-i\mathbf{k} \cdot \mathbf{s}) \int |k'|<k_F \exp(i\mathbf{k'} \cdot \mathbf{s}) \tag{16}
\]

\[
= -\frac{V}{64\pi^6} \int d^3\mathbf{s} \frac{1}{|s|} \left[ \int |k|<k_F \exp(i\mathbf{k} \cdot \mathbf{s}) \right] \left[ \int |k'|<k_F \exp(i\mathbf{k'} \cdot \mathbf{s}) \right] \tag{17}
\]

\[
= -\frac{V}{64\pi^6} \int d^3\mathbf{s} \frac{1}{|s|} \left| \int |k|<k_F \exp(i\mathbf{k} \cdot \mathbf{s}) \right|^2 = -\frac{V}{64\pi^6} \int d^3\mathbf{s} \frac{|X(k_F, \mathbf{s})|^2}{|s|} \tag{18}
\]

\[X(k_F, \mathbf{s}) = \int |k|<k_F \exp(i\mathbf{k} \cdot \mathbf{s}) = \int |k|<k_F \exp(i|\mathbf{k}||\mathbf{s}| \cos \theta)\]

\[X(k_F, s) = \int_0^{k_F} k^2 dk \int_0^\pi |\sin \theta| d\theta \int_0^{2\pi} d\varphi \exp(iks \cos \theta) = 2\pi \int_0^{k_F} dk \int_1^{-1} dx \exp(iksx) \tag{20}\]

\[= 2\pi \int_0^{k_F} k^2 dk \left[ \frac{1}{iks} \exp(iks) \right]^{1}_{-1} = \frac{4\pi}{s} \int k_F^k dk k^2 \left[ \exp(iks) - \exp(-iks) \right] \tag{21}\]

\[= \frac{4\pi}{s} \int_0^{k_F} dk k \sin(ks) = \frac{4\pi}{s} \left[ \frac{\sin(ks) - ks \cos(ks)}{s^2} \right] \tag{22}\]

\[E_x = -\frac{V}{64\pi^6} \int |s| \frac{|X(k_F, s)|^2}{|s|} = -\frac{16V^2}{64\pi^6} \int d^3\mathbf{s} \frac{|\sin(k_F s) - k_F s \cos(k_F s)|^2}{s^7} \tag{23}\]

\[= -\frac{V}{4\pi^4} 4\pi \int_0^{\infty} s^2 ds \frac{|\sin(k_F s) - k_F s \cos(k_F s)|^2}{s^7} \tag{24}\]

\[= -\frac{V}{\pi^4} \int_0^{\infty} (k_F s) \frac{|\sin(k_F s) - k_F s \cos(k_F s)|^2}{k_F s^7} \tag{25}\]

Again inserting the relation between the total density \( \rho \) and the Fermi momentum \( k_F = (3\pi^2 \rho)^{1/3} \) yields the energy functional

\[E_x[\rho] = -\frac{V}{4\pi^4} (3\pi^2)^{4/3} \rho^{4/3} = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} V \rho^{4/3} \tag{26}\]

### 1.5 Successful Application: Equilibrium Density of Metals

Combining the results from the two preceding sections the total energy of a homogeneous electron gas is given by

\[E[\rho] = T[\rho] + E_x[\rho] = \frac{3V}{10} (3\pi^2)^{2/3} \rho^{2/3} - \frac{3V}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{4/3} \tag{27}\]
In case of such homogeneous systems the background field (corresponding to the attractive nuclei) has to be constant and compensates exactly the Hartree potential. If not the system would either collapse (due to the stronger attraction of the background charge) or expand (due to the stronger repulsion of the electrons). Furthermore the system would have an infinite charge. For a charge neutral system we can thus ignore both terms in the expression for the total energy.

The kinetic energy is repulsive while the exchange energy is attractive. This results in an equilibrium state where both contributions are balanced. The corresponding equilibrium configuration can be calculated by differentiation of the total energy:

$$0 = \frac{\partial E}{\partial \rho} = \frac{3V}{10} \left( \frac{3\pi^2}{2} \right)^{2/3} \frac{5}{3} \rho^{2/3} - \frac{3V}{4} \left( \frac{3}{\pi} \right)^{1/3} \frac{4}{3} \rho^{1/3} \quad \Rightarrow \quad \rho = \frac{8}{3\pi^5} \approx 8.7 \times 10^{-3} \left[ \frac{1}{a_0^3} \right] \quad (28)$$

Typical electron densities inbetween the atoms of a metal (not at the atoms!!!) are about $10^{-3} - 10^{-2} a_0^{-3}$. Actually the good agreement with experimental data indicates that the valence electrons in a metal (which are the only ones which can be located inbetween the nuclei) are weekly bound and practically free particles. Plane waves – or corresponding free particles – have also been the initial model assumption of our derivations.

1.6 Inhomogeneous Systems and the Local Density Approximation (LDA)

$$E_x(\rho) = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int d^3r \, \rho^{4/3} \quad \Rightarrow \quad E_x[\rho] = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int d^3r \, \rho^{4/3}(r) \quad (29)$$

and similar for the kinetic energy functional

$$T[\rho] = \frac{3V}{10} \left( \frac{3\pi^2}{2} \right)^{2/3} \int d^3r \, \rho^{5/3}(r) \quad (30)$$

A spatial dependent density $\rho(r)$ allows to describe finite systems like isolated atoms and molecules. There the Hartree potential and the background field of the nuclei do not necessary have to cancel in each point of space.

1.7 Deficits of Thomas-Fermi Theory: Atoms and Molecules