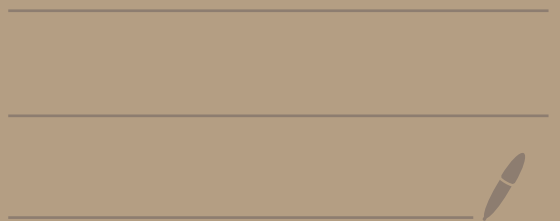


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22. Thomas-Fermi theory



## 22. The Thomas - Fermi theory

As we have seen, many of the problems are very difficult and complicated for the full many-body problem (stability, ground state energy, ionization ...).

The idea is to address them within the framework of simplified, effective theories.

An example of such effective theory is the Thomas - Fermi theory which describes the energy of a many-body quantum system only through its density

$$\rho(x) = N \int dx_2 \dots dx_N |\psi_N(x, x_2, \dots, x_N)|^2$$

(here  $\psi_N$  is the unknown many-body wave function).

Hence the name **density functional theory**.

TF theory is much easier to study than the full many-body problem, due to the fact that it depends on much less degrees of freedom (the density is a function on  $\mathbb{R}^3$ , while the wave function is a function on  $\mathbb{R}^{3N}$ ). Later we will discuss the validity of the TF approximation in the limit when  $N, \hbar \rightarrow \infty$ .

## 22.1. Derivation of TF functional

The starting point is the kinetic energy. We need to express it in terms of the density  $\rho$ .

To this end we consider the free Fermi gas.

To determine the kinetic energy of the free Fermi gas we know we need to fill the Fermi ball

$$N = \sum_{k < k_F} 1 \sim \int_{|k| < k_F} d^3k \sim k_F^3$$

the

$$E = \int_{|k| < k_F} k^2 d^3k \sim k_F^5 \sim N^{5/3}$$

If we make the assumption  $\rho(x) = \rho = N$ , the kinetic energy scales like  $\rho^{5/3}$ . Note that this scaling is in agreement with the semiclassical approximation, like the kinetic Lieb-Thirring bound.

Thus the one-body part of the TF functional will be given as

$$E_{TF}^{(1)}(\rho) = C_{TF} \int \rho(x)^{5/3} dx - \int \rho(x) V(x) dx$$

where  $V(x)$  is the electrostatic potential generated by the nuclei:

$$V(x) = \sum_{k=1}^M \frac{Z_k}{|x - R_k|}$$

Indeed, we have

$$\begin{aligned} \langle \varphi_N, \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|x_i - R_k|} \varphi_N \rangle &= \sum_{i=1}^N \sum_{k=1}^M z_k \int dx_1 \dots dx_N |\varphi_N(x_1, \dots, x_N)|^2 \frac{1}{|x_i - R_k|} \\ &= N \sum_{k=1}^M z_k \int dx_1 \dots dx_N |\varphi_N(x_1, \dots, x_N)|^2 \frac{1}{|x_i - R_k|} = \int dx \rho(x) V(x). \end{aligned}$$

For the electron-electron interaction we have:

$$\langle \varphi_N, \sum_{i < j} \frac{1}{|x_i - x_j|} \varphi_N \rangle$$

To make connection with the density  $\rho(x)$ , we assume the electrons are classical point particles with positions  $x_i$ . We treat them as independent, identically distributed random variables with probability distribution  $\rho(x)/N$ . Then

$$\frac{1}{N} \sum_{i \neq j} \frac{1}{|x_i - x_j|} \approx \int dx \frac{\rho(x)}{N} \frac{1}{|x_i - x|} \quad (*)$$

by the law of large numbers (on the left we have the mean energy experienced by the  $i$ -th particle

$$\frac{1}{N} (x_1 + \dots + x_N) \rightarrow \mu)$$

Under this approximation, we have

$$\langle \varphi_N, \sum_{i < j} \frac{1}{|x_i - x_j|} \varphi_N \rangle = \frac{1}{2} \langle \varphi_N, \sum_{i \neq j} \frac{1}{|x_i - x_j|} \varphi_N \rangle \approx$$

$$\approx \frac{1}{2} \langle \psi_N, \sum_{i=1}^N u(x_i) \psi_N \rangle$$

where  $u(x) = (g * 1 \cdot 1^{-1})(x)$ . The big conceptual simplification is that we replaced a sum of two-body operators by a sum of one-body operators by an averaging principle. Repeating the computation as for the external potential we get

$$\frac{1}{2} \langle \psi_N, \sum_{i=1}^N u(x_i) \psi_N \rangle = \frac{1}{2} \int dx dy \, g(x)g(y) \frac{1}{|x-y|}$$

All this leads to the Thomas-Fermi functional:

$$E_{TF}(g) = c_{TF} \int g^{5/3}(x) dx - \int g(x) V(x) dx + \frac{1}{2} \int \frac{g(x)g(y)}{|x-y|} dx dy + U$$

$$\text{where } V(x) = \sum_{j=1}^K \frac{z_j}{|x - R_j|}, \quad U = \sum_{i < j} \frac{z_i z_j}{|R_i - R_j|}$$

The domain of the functional is given by

$$\mathcal{F}_N = \{g: \mathbb{R}^3 \rightarrow \mathbb{R} \mid g(x) \geq 0, \|g\|_1 = N, g \in L^{5/3}(\mathbb{R}^3)\}$$

The Thomas-Fermi grand state energy:

$$E_N^{TF} = \inf_{g \in \mathcal{F}_N} E_{TF}(g)$$