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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 ψ_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 $N, Z \to \infty$.

22.1. Derivation of TF functional

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

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

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

$$\langle \varphi_N , \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{Z_k}{|x_i - R_k|} \varphi_N \rangle = \sum_{i=1}^{N} \sum_{k=1}^{M} Z_k \int dx_1 \dots dx_N \, |\varphi_N(x_1 \dots x_N)|^2 \frac{1}{|x_1 - R_k|}$$

$$= N \sum_{k=1}^{M} Z_k \int dx_1 \dots dx_N \, |\varphi_N(x_1, \dots, x_N)|^2 \frac{1}{|x_1 - R_k|} = \int dx \, \rho(x) V(x).$$

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 idependent, identically distributed random variables with probability distribution $\rho(x)/N$. Then

$$\frac{1}{N} \sum_{\substack{j \\ j \neq i}} \frac{1}{|x_i - x_j|} \simeq \int dx \, \frac{\rho(x)}{N} \frac{1}{|x_i - x|} \qquad (*)$$

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

$$\frac{1}{N}(X_1 + \dots + X_N) \to \mu).$$

Under this approximation, we have

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

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

where $\omega(x) = (\rho * |\cdot|^{-1})(x)$. 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

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

All this leads to the Thomas-Fermi functional:

$$\boxed{\mathcal{E}_{TF}(\rho) = c_{TF} \int \rho^{5/3}(x)\,dx - \int \rho(x) V(x)\,dx + \frac{1}{2} \int \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy + \mathcal{U}}$$

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

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

The Thomas-Fermi ground state energy:

$$\boxed{E_N^{TF} = \inf_{\rho \in \mathcal{F}_N} \mathcal{E}_{TF}(\rho)}$$