Problem set: Density functional theory

10.1. Functional derivatives

Consider the definition of functional derivative $\delta F[n]/\delta n(r)$ as

$$\lim_{\epsilon \to 0} \left[ \frac{F[n + \epsilon \delta n] - F[n]}{\epsilon} \right] = \int \frac{\delta F[n]}{\delta n(r)} \delta n(r) \, dr .$$

Calculate the functional derivative for the following functionals.

(a) The kinetic energy in the Thomas Fermi approximation

$$T_{TF}[n] = C \int n^{5/3}(r) \, dr .$$

(b) The Hartree energy

$$E_H[n] = \frac{e^2}{2} \int \int \frac{n(r) n(r')}{|r - r'|} \, dr \, dr' .$$

(c) The gradient correction of the kinetic energy in the Thomas Fermi approximation introduced by von Weizsäcker

$$T_W[n] = \frac{1}{8} \int \nabla n(r) \cdot \nabla n(r) \frac{n(r)}{n(r)} \, dr .$$

Hint: Use the Green’s theorem and take vanishing boundary conditions on a suitable surface.

10.2. Density functional theory in the Thomas Fermi approximation

Consider the total energy of an $N$ electron system in the Thomas Fermi approximation

$$E_{TF}[n] = T_{TF}[n] + E_H[n] + V[n] ,$$

where $T_{TF}[n]$ and $E_H[n]$ are given in the previous exercise and

$$V[n] = \int v(r) n(r) \, dr .$$
(a) By minimizing the total energy, formulate the corresponding density functional theory equations
\[ \frac{5}{3} [n(r)]^{2/3} + v_H(r) + v(r) = \mu . \]

\(v_H\) is the functional derivative of the Hartree energy.

(b) Repeat the same calculation for the case in which the electron density is described via
\[ n(r) = \begin{cases} 
A e^{-\lambda r} & \text{when } r < a \\
0 & \text{when } r > a 
\end{cases}, \]

where \(r = |r|\), \(a > 0\) and \(\lambda > 0\).